4

THE SCHRODINGER EQUATION

Intrduction

In Newtonian mechanics all dynamical variables such as position $\vec{r}(t)$, velocity $\vec{v}(t)$ etc. can be determined with absolute certainty. The governing equation in Newtonian mechanics is $\vec{F} = \frac{d\vec{p}}{dt} = m\frac{d^2\vec{r}}{dt^2}$. By solving this second order differential equation we can extract the entire history of the particle. History means the past, present and future of the particle. In most of the times we will be interested only in predicting the future values of dynamical variables. For solving the second order differential equation we require two boundary conditions. It may be initial position and velocity of the particle. Solving Newton's second law we get all the informations regarding the particle such as $\vec{r}(t)$, $\vec{v}(t)$, $\vec{a}$, energy even the trajectory of the particle. For example suppose a particle is under the influence of a force $\vec{F}$, we can go for solving Newton's second law. If the force is gravitational (a planet moves around the sun) we can write the equation of motion as

$$m\frac{d^2\vec{r}}{dt^2} = -\frac{GMm}{r^2}$$

solving this for getting the exact trajectory of the planet which is an elliptical path.

Now we come to quantum particles. Study of this comes under general name quantum mechanics. In quantum mechanics the basic (governing) equation is again a second order differential called schrödinger equation.

Unlike Newton's second law (which is expressed in terms of force), schrodinger equation is written in terms of energy. i.e., First one is force equation the second one is energy equation. Moreover solving schrodinger equation we do not get $r(t)$, $v(t)$ or trajectory of the particle but we get the wave function $\psi(\vec{r}, t)$ of the particle, which carries all the information regarding particles' wave like behaviour. In other words wave function encompasses all the informations regarding the particle. In this chapter we introduce schrodinger equation and learn how to solve it for some simple systems.

Behaviour of a wave at a boundary

We found that schrodinger equation is a second order differential equation. To solve it we require two boundary conditions. These conditions should come from the behaviour of matter waves at boundaries. Before analysing the behaviour of matter waves at the boundary, we recapitulate the behaviour of light waves and water waves at the boundaries.

Behaviour of light wave at boundary

Consider a light wave incident on a glass plate as shown in figure below.

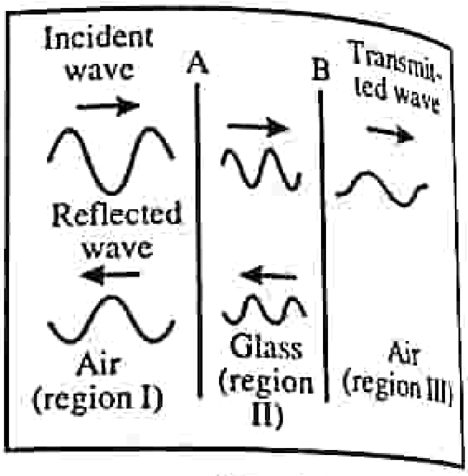


Figure 4.1

At the boundary A light travels from air (Region I) to glass (Region II). A the boundary some of the intensity is reflected back into air (Region I). The light wave enters into glass (region II) with less intensity the amplitude decreases. Since the speed of the wave in glass is less than that in air, the wavelength $(\lambda = v/\nu)$ of the light wave in glass (region II), decrease as frequency remains the same $\left(\lambda = \frac{v}{\nu}\right)$. At the boundary B some of the intensity is reflected back and the remaining light enters in to air (region III). Since the intensity decreases due to two former reflections, the amplitude of the wave in region III is small since $I \alpha a^2$. The wavelength of the light wave in region III is same as that in region I. Since $\lambda = \frac{c}{\nu}$ in both regions. As there is no boundary in the region III, there is no reflected wave.

Behaviour of water waves at the boundary

Consider three regions in water. Region I is deep, region II is shallow and region III is deep. Surface water waves enter from region I to region II. In region II the wavelength becomes smaller and amplitude becomes larger compared with original incident wave. When the wave enters the region III, in which depth is same as the region I, the wavelength returns to its original value but

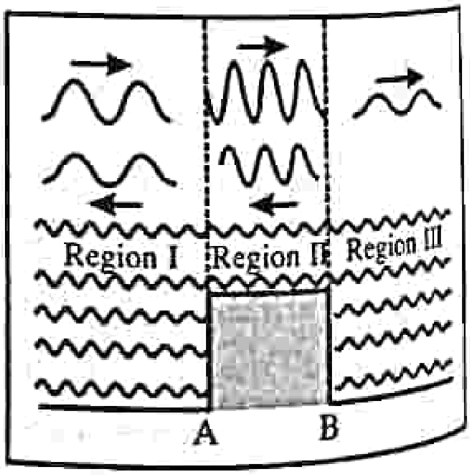


Figure 4.2

amplitude of the wave is smaller than the region I due to reflections at the boundaries.

Behaviour of matter waves at the boundary

Matter waves also exhibit the same type of behaviour as that of light waves and water waves. This time we consider three regions I, II and III. The region I and III are alike and separated by a negative potential energy - V_0.

Mathematically, the three regions are characterised by its potential energy (V).

$V = 0$ for region I

$V = -V_0$ for region II

$V = 0$ for region II

Consider that electrons are incident from region I and moving towards region II. Assume that initially (region I) the electrons have kinetic energy K.

$\therefore$ Its momentum $p = \sqrt{2mK}$ $\qquad \left(K = \dfrac{p^2}{2m}\right)$

Its de Broglie's wavelength $\lambda = \dfrac{h}{p} = \dfrac{h}{\sqrt{2mK}}$

We also assume that the original kinetic energy of the electrons in the region I is greater than V_0, so that electrons enter into the region II. There its kinetic energy become $K - V_0$, thus smaller momentum $p = \sqrt{2m(K - V_0)}$ and having greater wavelength, $\lambda = \sqrt{\dfrac{h}{2m(K - V_0)}}$.

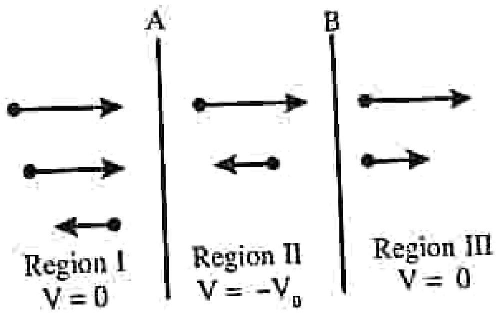


Figure 4.3

When the electrons move from region II to region III, they gain back the lost kinetic energy and move with original kinetic energy and original wavelength. In region III the amplitude of the matter wave in region III is smaller than region I because some of the electrons are reflected back at the boundaries A and B.

Note : In all three discussions of different waves we found there are 5 waves in the three regions. In region I two, region II two and region III only one.

Penetration of the reflected wave

Another property of classical waves shared by matter waves is the penetration of a totally reflected wave into a forbidden region. When a light wave is completely reflected from a boundary an exponentially decreasing wave called the evanescent wave penetrates into the second medium. Since 100% of the light wave is reflected, the evanescent wave carries no energy and so cannot be directly observed in the second medium. But if we make the second medium very thin of the order of few wavelengths of light the light wave can penetrate into the second medium. We will see this in detail later.

Like light waves matter waves can also penetrate into the forbidden region with exponentially decreasing amplitude. However, since matter waves are associated with electrons, electrons must penetrate into the forbidden region. But the electrons cannot be observed in the forbidden region because they have negative kinetic energy. But the effect producing electrons in the forbidden region can be experimentally observed.

Penetration of electrons in forbidden region can be explained on the basis of the uncertainty principle. According to uncertainty principle we can't know exactly the energy of the incident energy of electrons. We cannot say with certainty that electrons do not have enough kinetic energy to penetrate into the forbidden region. For a short interval of time Δt the uncertainty in energy $\Delta E \approx \frac{h}{\Delta t}$ might allow the electrons to penetrate into the forbidden region. We will discuss this also in detail later.

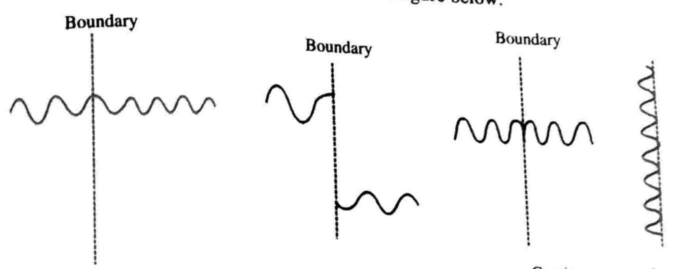
Continuity of waves at the boundaries

We know that the governing equation of a light wave or a water wave is a second order differential equation. The solution of this gives a function that represents the wave. Usually represented by $f(\bar{r}, t)$ called wave function.

The solution of this gives a function that represents the wave. Usually represented by $f(\bar{r}, t)$ called wave function. In the case of classical waves it is the displacement of the wave. For the matter waves it is the wave function $\psi(\bar{r}, t)$. To solve the second order differential equation completely we should know two boundary conditions. It comes from the two properties exhibited by waves at the boundaries. They are

1. The wave function must be continuous across each boundary.
2. The slope of the wave function must also be continuous at each boundary except the boundary height is infinite.

The continuity and discontinuity is shown in figure below.



Continuous wave function

Figure 4.4(a)

Discontinuous wave function

Figure 4.4(b)

Continuous wave but discontinuous slope

Figure 4.4(c)

When we apply two boundary conditions stated above to a light wave crossing three boundaries, we have

$$(f_I)_A = (f_{II})_A \qquad \text{..... (1)}$$

where f_I is the wave function in the region I. $(f_I)_A$ is the wave function in the region I at the boundary A.

Similarly
$$(f_{II})_B = (f_{III})_B \qquad \text{..... (2)}$$

By applying the condition on slope, we can write

$$\left(\frac{\partial f_I}{\partial x}\right)_A = \left(\frac{\partial f_{II}}{\partial x}\right)_A \qquad \text{..... (3)}$$

and
$$\left(\frac{df_{II}}{dx}\right)_B = \left(\frac{df_{III}}{dx}\right)_B \qquad \text{..... (4)}$$

Using equations 1, 2, 3 and 4 we can determine the two constants in the solution $f(x, t)$. In the case of sound waves or light waves these constants are amplitude and phase of the wave.

These boundary conditions can equally be applied to matter waves.

So far we learnt three properties of classical waves that also apply to matter waves. They are

1. When a wave crosses a boundary between two regions, part of the wave is reflected and part is transmitted.
2. When a wave encounters a boundary to a region from which it is forbidden, the wave may penetrate into the forbidden region by a few wavelengths.
3. At a finite boundary the wave and its slope are continuous. At an infinite boundary its slope is discontinuous.

Example 1

A wave has the form $y = A\cos\left(\frac{2\pi x}{\lambda} + \frac{\pi}{3}\right)$, when $x < 0$. For $x > 0$, the wavelength is $\frac{\lambda}{2}$. By applying continuity conditions at $x = 0$, find the amplitude in terms of A and phase of the wave in the region $x > 0$.

Solution

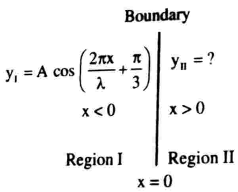


Figure 4.5

$$y_I = A\cos\left(\frac{2\pi x}{\lambda} + \frac{\pi}{3}\right)$$

In the region II, we assume that

$$y_{II} = A_1\cos\left(\frac{2\pi x}{\lambda_1} + \phi\right)$$

Applying the first boundary condition, we get

$$(y_I)_{x=0} = (y_{II})_{x=0}$$

i.e.,

$$\left[A\cos\left(\frac{2\pi x}{\lambda} + \frac{\pi}{3}\right)\right]_{x=0} = \left[A_1\cos\left(\frac{2\pi x_1}{\lambda_1} + \phi\right)\right]_{x=0}$$

$$A\cos\frac{\pi}{3} = A_1\cos\phi$$

or

$$\frac{A}{2} = A_1\cos\phi \qquad \text{..... (1)}$$

Applying the second boundary condition, we get

$$\left(\frac{dy_I}{dx}\right)_{x=0} = \left(\frac{dy_{II}}{dx}\right)_{x=0}$$

$$\left[-A\sin\left(\frac{2\pi x}{\lambda} + \frac{\pi}{3}\right)\cdot\frac{2\pi}{\lambda}\right]_{x=0} = \left[-A_1\sin\left(\frac{2\pi x_1}{\lambda_1} + \phi\right)\frac{2\pi}{\lambda_1}\right]_{x=0}$$

$$A\sin\frac{\pi}{3}\cdot\frac{2\pi}{\lambda} = A_1\sin\phi\cdot\frac{2\pi}{\lambda_1}$$

or

$$\frac{A\sqrt{3}}{2\lambda} = \frac{A_1}{\lambda_1}\sin\phi \qquad \text{..... (2)}$$

or

$$\frac{A_1\cos\phi}{\lambda}\sqrt{3} = \frac{A_1}{\lambda_1}\sin\phi$$

But $\lambda_1 = \frac{\lambda}{2}$ given

$\therefore$ $\sqrt{3}\cos\phi = 2\sin\phi$

$$\phi = \tan^{-1}\left(\frac{\sqrt{3}}{2}\right) = 40.89^\circ$$

Putting this in equation (1), we get

$$A_1 = \frac{A}{2\cos 40.89} = 0.661\,A$$

Example 2

A wave is crossing three regions separated by two boundaries A and B. The boundary A is at $x = 0$ and boundary B is at $x = 20.0$cm. The wave in region I is given by $y_I(x) = 5\sin\left(\pi x - \frac{\pi}{6}\right)$. In region II the wavelength $\lambda = 4$cm. Find the wave function in region III.

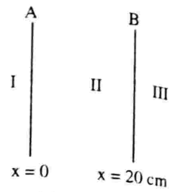


Figure 4.6

Solution

$$y_I = 5\sin\left(\pi x - \frac{\pi}{6}\right)$$

In the region II, we assume that

$$y_{II} = A_1 \sin\left(\frac{2\pi x}{4} - \phi_1\right)$$

Using $(y_I)_{x=0} = (y_{II})_{x=0}$

$$-5\sin\frac{\pi}{6} = -A_1 \sin\phi_1$$

$$\frac{5}{2} = A_1 \sin\phi_1 \qquad .....(1)$$

We also have

$$\left(\frac{dy_I}{dx}\right)_{x=0} = \left(\frac{dy_{II}}{dx}\right)_{x=0}$$

$$\left[5\cos\left(\pi x - \frac{\pi}{6}\right)\cdot\pi\right]_{x=0} = \left[A_1\cos\left(\frac{2\pi x}{4} - \phi_1\right)\cdot\frac{2\pi}{4}\right]_{x=0}$$

$$5\pi\cos\left(\frac{-\pi}{6}\right) = A_1\cos(-\phi_1)\frac{\pi}{2}$$

$$\frac{5\sqrt{3}}{2} = A_1\cos\phi_1\frac{1}{2}$$

$$5\sqrt{3} = A_1\cos\phi_1 \qquad .....(2)$$

$\frac{eq(1)}{eq(2)}$ gives

$$\frac{\sqrt{3}}{2} = \tan\phi_1$$

$$\phi_1 = \tan^{-1}\frac{\sqrt{3}}{2} = 40.9^\circ$$

$$\therefore \quad A_1 = \frac{5\sqrt{3}}{\cos 40.9} = 11.46\text{cm}$$

$$\therefore \quad y_{II} = 11.46\sin\left(\frac{2\pi x}{4} - 40.9^\circ\right)$$

To find the wave function in region III, we assume the form

$$y_{III} = A_2\sin(\pi x - \phi_2)$$

we have $(y_{II})_{x=20} = (y_{III})_{x=20}$

$$11.46\sin(10\pi - 40.9^\circ) = A_2\sin(20\pi - \phi_2)$$

i.e., $11.46\sin 40.9^\circ = -A_2\sin\phi_2$

or $7.5 = A_2\sin\phi_2 \qquad .....(3)$

Using $\left(\frac{dy_{II}}{dx}\right)_{x=20} = \left(\frac{dy_{III}}{dx}\right)_{x=20}$

$$\left[11.46\cos\left(\frac{2\pi x}{4} - 40.9^\circ\right)\cdot\frac{2\pi}{4}\right]_{x=20} = [A_2\cos(\pi x - \phi_2)\cdot\pi]_{x=20}$$

$$11.46\cos 40.9^\circ\cdot\frac{\pi}{2} = A_2\cos\phi_2\cdot\pi$$

or $4.33 = A_2\cos\phi_2 \qquad .....(4)$

$\frac{eq\,4}{eq\,3}$ gives $\tan\phi_2 = \frac{7.5}{4.33} = 1.732$

$$\phi_2 = 60^\circ$$

and $A_2 = \dfrac{4.33}{\cos 60^\circ} = 8.66$

$$\therefore \quad y_{III} = 8.66 \sin\left(\pi x - \frac{\pi}{3}\right)$$

Note : How does the amplitude of region II is greater than that in region I. This is because when we write a wave in region I it includes the incident as well as reflected.

Confining a particle

A particle is said to be free if it experiences no force of any kind or potential energy. Such a particle has definite wavelength, momentum and energy. Moreover any value can be given to it. On the other hand when a particle is subjected to an external potential energy so that the particle is confined to the region in which potential exists is called a confined particle.

A confined quantum particle is represented by a wave packet which makes the particle confine to a small region of space.

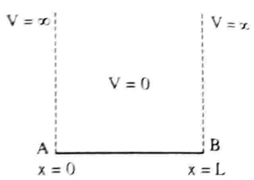


Figure 4.7

Consider a quantum particles (electron) is confined to a region $x = 0$ to $x = L$. We assume that at the two boundaries, potential energy is infinite and potential energy is zero inside. This assumption is made so that the particle's kinetic energy is low when compared to potential energy at the boundaries. In this case the penetration into the forbidden region cannot occur. The probability to find the electron in either side regions is zero. So also the wave amplitudes in those regions including at the boundaries A and B.

The particle is represented by matter waves, so the wave function must obey the boundary conditions at $x = 0$ and $x = L$. The possible waves are given in figure 4.8.

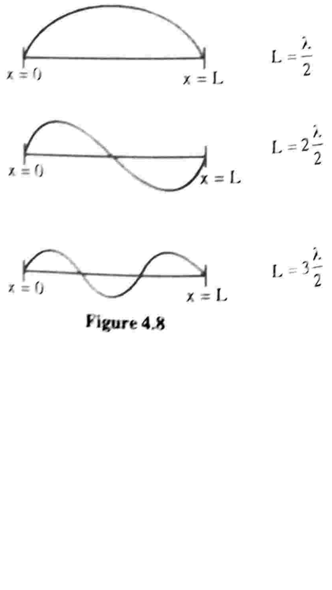


Figure 4.8

In general we can write $L = \dfrac{n\lambda}{2}$, $n = 1, 2, \ldots$

or $$\lambda = \frac{2L}{n} \qquad n = 1, 2, 3, \ldots$$

or $$\lambda_n = \frac{2L}{n} \qquad n = 1, 2, 3, \ldots$$

From Debroglie wavelength $\lambda = \dfrac{h}{p}$

$$p = \frac{h}{\lambda}$$

or $$p_n = \frac{h}{\lambda_n} \qquad \ldots\ldots (5)$$

Substituting for λ_n, we get

$$p_n = n\frac{h}{2L}, \quad n = 1, 2, 3, \ldots \qquad \ldots\ldots (6)$$

$\therefore$ kinetic energy of the particle, $E_n = \dfrac{p_n^2}{2m}$

$$E_n = \frac{n^2 h^2}{8m\,L^2} \quad n = 1, 2, 3, \ldots \qquad \ldots\ldots (7)$$

Equations 6 and 7 show that only certain values of momentum and energy are permitted to take by the particle when it is confined. In other words momentum and energy are quantized. Quantization of momentum and energy are the principal features of quantum theory. By studying the quantizated energy levels of quantum systems we can gather informations regarding atoms and nuclei. This is the technique used by experimental scientists.

Example 3

The lowest energy of a particle in an infinite one dimensional well is 4.4eV. If the width of the well is doubled. What is its lowest energy.

Solution

We have $E_n = \frac{n^2h^2}{8mL^2}$

For lowest energy $n = 1$

$$E_1 = \frac{h^2}{8mL^2} = 4.4\text{eV}$$

When the width of the level is doubled

$$E_1^! = \frac{h^2}{8m(2L)^2} = \frac{h^2}{4\ 8mL^2} = \frac{1}{4}\times 4.4$$

$$E_1^! = 1.1\text{eV}.$$

Example 4

An electron is trapped in an infinite well of width 0.120nm. What are the three longest wavelengths permitted for electrons de Broglie waves

Solution

We have $\lambda_n = \frac{2L}{n}$

for $n = 1,\ \lambda_1 = 2L = 2\times 0.12 = 0.240\text{nm}$

for $n = 2,\ \lambda_2 = L = 0.120\text{nm}$

for $n = 3,\ \lambda_3 = \frac{2L}{3} = \frac{2\times 0.12}{3} = 0.80\text{nm}.$

Applying the uncertainty principle to a confined particle

Consider a particle confined to a length L. Its uncertainty in position is $\Delta x = L$. Uncertainty in momentum is

$$\Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2}$$

But the average momentum of the particle $\langle p_x\rangle = 0$

Thus $\Delta p_x = \sqrt{\langle p_x^2\rangle}$

But we already have $p_x = \frac{nh}{L}$

$$\therefore \quad p_x^2 = \frac{n^2h^2}{L^2}$$

$$\langle p_x^2\rangle = \frac{n^2h^2}{L^2}$$

$$\therefore \quad \Delta p_x = \frac{nh}{L}$$

Now we calculate the product of $\Delta x\, \Delta p_x$

i.e., $\Delta x\, \Delta p_x = L\cdot\frac{nh}{L}$

$$\Delta x\, \Delta p_x = nh$$

This is in perfect agreement with the uncertainty principle stating that

$$\Delta x\, \Delta p_x \geq \frac{\hbar}{2}$$

Since $nh \geq \frac{\hbar}{2}$ for all values of n.

The Schrödinger equation

Soon after the publication of de Broglie's hypothesis Erwin Schrödinger in 1926 proposed that the behaviour of matter waves associated with material particles is governed by a second order differential equation called Schrödinger equation. The solution of the differential equation is the wave function which gives us the wave behaviour of particles. Schrödinger developed this into a rigorous mathematical theory known as wave mechanics. Here our aim is to set up Schrödinger equation and their properties. Schrödinger equation cannot be derived from any fundamental principles like Newton's laws. But the justification comes from the experimental observations at atomic and sub atomic level.

Development of Schrödinger equation

Let $\psi(x, t)$ be the wave function representing wave behaviour of particles (matter waves). Consider a matter wave

$$\psi(x, t) = A \sin(kx - \omega t)$$

Suppressing time factor and write it as

$$\psi(x) = A \sin kx \qquad \text{..... (8)}$$

where A is the amplitude and $k = \left(\frac{2\pi}{\lambda}\right)$ is the wave vector of the wave.

We require a second order differential equation whose solution is $\psi(x)$.

Differentiating eqution (8) twice, we get

$$\frac{d\psi}{dx} = kA\cos kx$$

$$\frac{d^2\psi}{dx^2} = -k^2 A \sin kx$$

or $$\frac{d^2\psi}{dx^2} = -k^2\psi(x) \qquad \text{..... (9)}$$

From kinetic energy expression

$$K = \frac{p^2}{2m} = \frac{\left(\frac{h}{\lambda}\right)^2}{2m} = \frac{h^2}{2m\,\lambda^2} \qquad \left(\because p = \frac{h}{\lambda}\right)$$

$$K = \frac{h^2}{4\pi^2 \cdot 2m}\,\frac{4\pi^2}{\lambda^2}$$

$$K = \frac{\hbar^2 k^2}{2m}$$

Using $k^2 = \frac{2m}{\hbar^2} K$

total energy, = kinetic energy + potential energy

$$E = K + V(x)$$

or $$K = E - V(x)$$

Thus $$k^2 = \frac{2m}{\hbar^2}\ (E - V(x))$$

Put the value of k^2 in equation 9, we have

$$\frac{d^2\psi}{dx^2} = \frac{-2m}{\hbar^2}\ (E - V(x)\psi(x)$$

or $$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi - V(x)\psi(x)$$

or $$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad \text{..... (10)}$$

This is the time independent Schrödinger equation for one dimensional motion. Remember that our matter wave is the wave associated with a moving particle so it must be time dependent. i.e., wave function must involve x and t. This wave is represented by

$$\underline{\psi}(x, t) = \psi(x)e^{-i\omega t} \qquad \text{..... (11)}$$

where $$\omega = \frac{E}{\hbar}$$

(For more rigorous derivation of Schrödinger equation see appendix C).

Now our aim is to solve Schrödinger equation for a known potential energy $V(x)$. Solving we get $\psi(x)$ and energy values of the particle.

Equation 10 can be written as

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x)$$

or $$\hat{H}\psi(x) = E\psi(x) \qquad \text{..... (12)}$$

where $$\hat{H} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

Equation 12 is like our eigen value equation $AX = \lambda X$. Thus solving Schrödinger equation implies solving eigen value problem. The energy values so obtained are called energy eigen values.

The general procedure for solving Schrödinger equation

Step I

Write down the Schrödinger equation with the appropriate potential energy.

Step II

Solve the second order differential equation to get $\psi(x)$ by using any mathematical technique.

Step III

In general several solutions are obtained. By applying boundary conditions the actual solutions and the arbitrary constants may be determined. Finally find the energy eigen values.

Note : If the given potential energy is discontinuous apply the continuity conditions on $\psi(x)$ and $\frac{d\psi}{dx}$ at the boundary between different regions.

Don't think that now the solution $\psi(x)$ is complete. For completing the solution we also have to determine the amplitude A of the wave function, this comes from the concept of probability.

Probability and normalisation

Wave function plays a key role in quantum mechanics even though it is not a physically measurable one. This is because wave function encompasses all the informations regarding the particle. The wave function ψ is called probability amplitude which is not physically measurable but square of its absolute magnitude $|\psi|^2$ evaluated at a particular place and at a particular time gives the probability density so $|\psi|^2 dx$ gives the probability of finding the particle within the interval dx at x.

If we define $P(x)$ as the probability density (probability per unit length in one dimension), then

$P(x)dx = |\psi|^2 dx$ by definition. In general $\psi(x)$ is complex so squaring $\psi(x)$ means

$$\psi^*(x)\psi(x) = |\psi(x)|^2$$

So, the total probability of finding the particle between $-\infty$ to ∞ is given by

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx$$

Since the probability of finding the particle in a given overall length is unity, we can write

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \qquad \text{.....(13)}$$

This condition is called normalisation condition. The wave function which satisfies eq (13) is said to be a normalised wave function.

If the probability of finding the particle in overall length is zero.

i.e., $$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 0$$

This means that the particle does not exist.

The limit of integration given above ($-\infty$ and ∞) simply indicates the domain of the wave function exists. If the particle is restricted in one dimension between x_1 and x_2, the probability is given by

$$\int_{x_1}^{x_2} |\psi(x)|^2 dx$$

The normalisation condition along with the 4 steps we discussed earlier will enable us to complete the solution of the Schrödinger equation.

If we consider time dependent wave function $\underline{\psi}(x, t) = \psi(x)e^{-i\omega t}$

then $$|\underline{\psi}(x, t)|^2 = \underline{\psi}^*(x, t)\underline{\psi}(x, t)$$

$$= \psi^*(x)e^{i\omega t}\psi(x)e^{-i\omega t}$$

$$|\underline{\psi}(x, t)|^2 = \psi^*(x)\psi(x) = |\psi(x)|^2$$

This shows that probability density is independent of time. Such states are called stationary states.

A state with a well defined energy which has a wave function of the form $\psi(x)e^{-i\omega t}$ and for such state the probability density is independent of time is called a stationary state.

Expectation values

The interpretation of the square of the wave function as the probability density makes it possible to calculate the average or expectation value $\langle x \rangle$ of the position of the particle. The expression $|\psi|^2\,dx$ gives only the probability of finding the particle in between x and $x+dx$. So what we do is make large number of observations of the particle (we do not expect the same value in each time), then take the mean of all observed values of position. This is called mean value or expectation value of the position.

Definition

The expectation value of a dynamical quantity is the mathematical expectation for the result of a single measurement. Or it is defined as the average of the results of a large number of measurements on independent identical systems i.e., the systems represented by identical wave functions.

Expression for the expectation value of position $\langle x \rangle$

Let us find the expectation value $\langle x \rangle$ at time t of the position of an electron along the x-axis in an experimental arrangement such as electron diffraction experiment. Suppose we study the positions of a large number of electrons N all of which are described by the same wave function $\psi(x, t)$. Suppose at time t, for each electron, we make an observation for the electron's position and find the number of electrons with positions between x and $x+dx$. Then the probability of a electron will be in the position between x and $x+dx$,

$$P = \frac{\text{Number of electrons in the positions between } x \text{ and } x+dx}{N} \quad \text{..... (1)}$$

But according to the interpretation of the wave function, this probability P is

$$P = \psi^*(x, t)\,\psi(x, t)dx \quad \text{..... (2)}$$

Assume that ψ is normalised.

From equations (1) and (2), we get

Number of electrons in the positions between x and $x+dx = N\psi^*\psi dx$.

Hence the sum of all the measured values $x_1, x_2, \cdots x_N$ for all the N electrons is given by

$$x_1 + x_2 + \ldots\ldots x_N = \int_{-\infty}^{\infty} N x \psi^* \psi dx$$

$$\therefore \quad \frac{x_1 + x_2 + \ldots\ldots x_N}{N} = \int_{-\infty}^{\infty} x \psi^* \psi dx$$

The left hand side of this equation is the expectation value $\langle x \rangle$

$$\therefore \quad \langle x \rangle = \int_{-\infty}^{\infty} \psi^* x \psi dx \quad \text{..... (1)}$$

In a similar way the expectation value of any dynamical quantity $f(x)$ is given by

$$\langle f(x) \rangle = \int_{-\infty}^{\infty} \psi^* f(x) \psi dx \quad \text{..... (2)}$$

The expectation value of potential energy $V(x)$ is given by

$$\langle V \rangle = \int_{-\infty}^{\infty} \psi^*\, V(x) \psi dx \quad \text{..... (3)}$$

Example 5

Normalise the wave function $\psi(x) = e^{-\frac{x}{a}}$

Solution

Let the normalised wave function be $A\psi$,

$$\text{then} \int_{-\infty}^{\infty} (A\psi)^* (A\psi)\, dx = 1$$

i.e.,

$$|A|^2 \int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

$$|A|^2 \int_{-\infty}^{\infty} e^{-\frac{x}{a}} e^{-\frac{x}{a}} dx = 1, \quad |A|^2 \int_{-\infty}^{\infty} e^{-2\frac{x}{a}} dx = 1$$

or

$$|A|^2\, 2\int_{0}^{\infty} e^{-2\frac{x}{a}} dx = 1, \quad |A|^2\, 2\left[\frac{e^{-2\frac{x}{a}}}{-\frac{2}{a}}\right]_0^{\infty} = 1$$

$$-a|A|^2 [e^{-\infty} - e^0] = 1, \quad a|A|^2 = 1, \quad |A| = \frac{1}{\sqrt{a}}$$

$\therefore$ The normalised wave function is

$$\psi(x) = \frac{1}{\sqrt{a}} e^{-\frac{x}{a}}$$

Example 6

Normalise the wave function $\psi(x) = \sin kx$ between $-\frac{L}{2}$ to $\frac{L}{2}$ with $k = \frac{n\pi}{L}$

Solution

Let $A\psi$ be the normalised wave function, then we have

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} (A\psi)^* A\psi \, dx = 1$$

$$|A|^2 \int_{-\frac{L}{2}}^{\frac{L}{2}} \psi^* \psi \, dx = 1$$

$$|A|^2 \int_{-\frac{L}{2}}^{\frac{L}{2}} \sin^2 kx \, dx = 1$$

$$|A|^2 \int_{-\frac{L}{2}}^{\frac{L}{2}} \left(\frac{1 - \cos 2kx}{2} \right) dx = 1$$

$$\frac{|A|^2}{2} \left[\int_{-\frac{L}{2}}^{\frac{L}{2}} 1 dx - \int_{-\frac{L}{2}}^{\frac{L}{2}} \cos 2kx \, dx \right] = 1$$

$$\frac{|A|^2}{2} \left\{ [x]_{-\frac{L}{2}}^{\frac{L}{2}} - \left[\frac{\sin 2kx}{2k} \right]_{-\frac{L}{2}}^{\frac{L}{2}} \right\} = 1$$

$$\sin 2kx \Big|_{-\frac{L}{2}}^{\frac{L}{2}} = \sin 2k\frac{L}{2} - \sin 2k - \frac{L}{2}$$

$$= \sin kL + \sin kL = 2 \sin kL$$

$$= 2 \sin \frac{n\pi}{L} L = 0$$

$\therefore$ we get

$$\frac{|A|^2}{2} L = 1$$

or $$A = \sqrt{\frac{2}{L}}$$

Therefore the normalised wave function is

$$\psi(x) = \sqrt{\frac{2}{L}} \sin kx$$

Example 7

Normalise the wave function $\psi(x) = e^{-\frac{m\omega}{2\hbar}x^2}$. Given that $\int_{-\infty}^{\infty} e^{-t^2} dt = \sqrt{\pi}$

Solution

Let $A\psi$ be the normalised eigen function, then we have

$$|A|^2 \int_{-\infty}^{\infty} e^{-2\alpha x^2} dx = 1 \qquad \text{.....(1)}$$

where $$\alpha = \frac{m\omega}{2\hbar}$$

Put $2\alpha x^2 = t^2$ $\qquad \therefore 2\alpha \, 2x \, dx = 2t dt$

$$dx = \frac{t\,dt}{2x\alpha} = \frac{t\,dt}{\frac{2\alpha t}{\sqrt{2\alpha}}} \qquad \therefore dx = \sqrt{\frac{1}{2\alpha}} dt$$

Now eqn (1) becomes

$$|A|^2 \sqrt{\frac{1}{2\alpha}} \int_{-\infty}^{\infty} e^{-t^2} dt = 1$$

$$|A|^2 \sqrt{\frac{1}{2\alpha}} \sqrt{\pi} = 1$$

$$|A|^2 = \sqrt{\frac{2\alpha}{\pi}}$$

or $$|A| = \left(\frac{2\alpha}{\pi}\right)^{\frac{1}{4}} = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$$

∴ The normalised wave function is

$$\psi(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}$$

Example 8

Find the expectation value of position of a particle whose wave function is $\psi(x) = Ne^{-\frac{x^2}{2a^2}+ikx}$

Solution

We have $$\langle x\rangle = \int_{-\infty}^{\infty} x\psi^*\psi dx$$

$$\langle x\rangle = |N|^2 \int_{-\infty}^{\infty} e^{-\frac{x^2}{a^2}} x dx$$

Since the intergrand is an odd function, the integral vanishes

∴ $$\langle x\rangle = 0$$

Example 9

Find the expectation value of momentum of a particle whose wave function is

$$\psi(x) = Ne\int_{-\infty}^{\infty} e^{-\frac{x^2}{2a^2}+ikx}$$

Solution

We have

$$\langle p\rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi dx$$

$$\langle p\rangle = \int_{-\infty}^{\infty} \psi^*\left(-i\hbar\frac{d}{dx}\right)\psi dx$$

$$\langle p\rangle = -i\hbar\int_{-\infty}^{\infty} \psi^*\frac{d}{dx}\psi dx \qquad \text{.....(1)}$$

$$\frac{d\psi}{dx} = \frac{d}{dx}\left(Ne^{-\frac{x^2}{2a^2}+ikx}\right) = N\frac{d}{dx}\left(e^{-\frac{x^2}{2a^2}+ikx}\right)$$

$$= N\left(-\frac{x}{a^2}+ik\right)e^{-\frac{x^2}{2a^2}+ikx}$$

$$\psi^* = N^* e^{-\frac{x^2}{2a^2}-ikx}$$

putting $\frac{d\psi}{dx}$ and ψ^* in eq (1), we get

$$\langle p\rangle = -i\hbar|N|^2\int_{-\infty}^{\infty}\left(-\frac{x}{a^2}+ik\right)e^{-\frac{x^2}{a^2}}dx$$

$$\langle p\rangle = +\frac{i\hbar|N|^2}{a^2}\int_{-\infty}^{\infty} xe^{-\frac{x^2}{a^2}}dx + \hbar|N|^2 k\int_{-\infty}^{\infty} e^{-\frac{x^2}{a^2}}dx$$

The first integral vanishes since the integrand is odd

$$\langle p\rangle = \hbar k\int_{-\infty}^{\infty}|N|^2 e^{-\frac{x^2}{a^2}}dx$$

or $$\langle p\rangle = \hbar k\int_{-\infty}^{\infty}\psi^*\psi dx$$

∴ $$\langle p\rangle = \hbar k \qquad \left(\because \int_{-\infty}^{\infty}\psi^*\psi dx = 1\right)$$

Example 10

In the region $0 \le x \le a$, a particle is described by the wave function $\psi_1(x) = -b(x^2 - a^2)$. In the region $a \le x \le \omega$ its wave function is $\psi_2(x) = (x-d)^2 - c$. For $x \ge \omega$, $\psi_3(x) = 0$ (a) By applying boundary conditions at $x = a$, find c and d in terms of a and b. (b) Find ω in terms of a and b

Solution

$$\psi_1(x) = -b(x^2 - a^2)$$

$$\psi_2(x) = (x-d)^2 - c$$

$$\psi_3(x) = 0$$

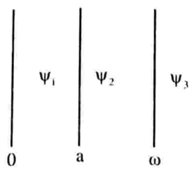


Figure 4.9

Using $\quad \psi_1(x)\Big|_{x=a} = \psi_2(x)\Big|_{x=a}$

$$0 = (a-d)^2 - c$$

giving $(a-d)^2 = c$ ..... (1)

and $\dfrac{d\psi_1}{dx}\Big|_{x=a} = \dfrac{d\psi_2}{dx}\Big|_{x=a}$

$$-2bx\Big|_{x=a} = 2(x-d)\Big|_{x=a}$$

$$-2ba = 2(a-d)$$

$\therefore \quad a - d = -ab$ ..... (2)

Putting this in eq (1), we get

$$a^2b^2 = c$$

From eq 2, we get $d = a(1+b)$

(b) $\quad \psi_2(x)\Big|_{x=\omega} = \psi_3(x)\Big|_{x=\omega}$

$$(x-d)^2 - c\Big|_{x=\omega} = 0$$

$$(\omega - d)^2 - c = 0$$

or $\quad \omega - d = \sqrt{c}$

$$\omega = \sqrt{c} + d$$

$$\omega = a\ b + a(1+b)$$

$$\omega = a\ (b+1)$$

Example 11

A particles is represented by the following wave function

$$\psi(x) = 0 \qquad x < \frac{-L}{2}$$

$$= c\left(\frac{2x}{L} + 1\right) \qquad \frac{-L}{2} < x < 0$$

$$= c\left(\frac{-2x}{L} + 1\right) \qquad 0 < x < \frac{L}{2}$$

$$= 0 \qquad x > \frac{L}{2}$$

Find c using normalisation condition.

Solution

The domain of $\psi(x)$ is from $\dfrac{-L}{2}$ to $\dfrac{L}{2}$. Using normalisation condition, we have

$$\int_{-L/2}^{L/2} |\psi(x)| dx = 1$$

i.e., $\quad \displaystyle\int_{-L/2}^{0} |\psi|\, dx + \int_{0}^{L/2} |\psi|^2\, dx = 1$

$$\int_{-L/2}^{0} cc^*\left(\frac{2x}{L} + 1\right)^2 dx + \int_{0}^{L/2} cc^*\left(\frac{-2x}{L} + 1\right)^2 dx = 1$$

$$|c|^2 \int_{-L/2}^{0} \left(\frac{4x^2}{L^2} + \frac{4x}{L} + 1\right) dx + |c|^2 \int_{0}^{L/2} \left(\frac{4x^2}{L^2} - \frac{4x}{L} + 1\right) dx = 1$$

$$|c|^2\left[\left(\frac{4x^3}{3L^2}+\frac{4x^2}{2L}+x\right)\Bigg|_{-L/2}^{0}+\left(\frac{4x^3}{3L^2}-\frac{4x^2}{2L}+x\right)\Bigg|_{0}^{L/2}\right]=1$$

$$|c|^2\left[\left(\frac{4}{3}\frac{L^3}{8L^2}-\frac{L^2}{2L}+\frac{L}{2}\right)+\left(\frac{4L^3}{3\cdot 8L^2}-\frac{L^2}{2L}+\frac{L}{2}\right)\right]$$

$$|c|^2\left[\left(\frac{1}{6}L-\frac{L}{2}+\frac{L}{2}\right)+\frac{L}{6}-\frac{L}{2}+\frac{L}{2}\right]=1$$

$$|c|^2\frac{L}{3}=1$$

$$\therefore \qquad |c|=\sqrt{\frac{3}{L}}$$

Applications of Schrödinger equation

Solutions for constant potential energy

Consider a particle subjected to a constant potential energy V_0 moving in one dimension. The Schrödinger equation of this particle is given by

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+V_0\psi(x)=E\psi(x)$$

or
$$\frac{d^2\psi(x)}{dx^2}-\frac{2m}{\hbar^2}V_0\psi(x)=\frac{-2m}{\hbar^2}E\psi(x)$$

or
$$\frac{d^2\psi(x)}{dx^2}=\frac{-2m}{\hbar^2}(E-V_0)\psi(x) \qquad \text{..... (14)}$$

Here our aim is to solve this Schrodinger equation.

Case I

If $E > V_0$

When E is greater than V_0, the term $\frac{2m}{\hbar^2}(E-V_0)$ is a positive quantity

Let $\frac{2m}{\hbar^2}(E-V_0)=k^2$

Now equation 14 becomes

$$\frac{d^2\psi(x)}{dx^2}=-k^2\psi(x) \qquad \text{..... (15)}$$

The solution of the equation 15 is

$$\psi(x)=A\sin kx+B\cos kx$$

The constants A and B can be determined by applying boundary conditions and the normalisation condition

Case II

If $E < V_0$

When E is less than V_0, the term $\frac{2m}{\hbar^2}(E-V_0)$ is negative. Take $\frac{2m}{\hbar^2}(V_0-E)$ which is positive, let it be k'^2

i.e., $$\frac{2m}{\hbar^2}(V_0-E)=k'^2$$

Now our Schrodinger equation 14 becomes

$$\frac{d^2\psi(x)}{dx^2}=k'^2\psi(x) \qquad \text{..... (16)}$$

The general solution of this equation is

$$\psi(x)=Ce^{k'x}+De^{k'x} \qquad \text{..... (17)}$$

As before we can determine C and D by applying boundary conditions and normalisation condition.

The case 2 $E < V_0$ will enable us to analyse the penetration of a particle into forbidden region.

The free particle

A free particle experiences no force at all. $F=0$, implies $\frac{-dV}{dx}=0$ since $F=\frac{-dV}{dx}$. $F=0$, means that the potential energy is constant or zero. We already considered the case of constant potential energy, so we assume that $V=0$.

Now our Schrödinger equation becomes

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

or $$\frac{d^2\psi(x)}{dx^2} = \frac{-2mE}{\hbar^2}\psi(x)$$

put $$\frac{2mE}{\hbar^2} = k^2 \qquad \text{..... (18)}$$

$\therefore$ $$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \qquad \text{..... (19)}$$

The general solution is

$$\psi(x) = A\sin kx + B\cos kx$$

From equation (18), we can write

$$E = \frac{\hbar^2 k^2}{2m} \qquad \text{..... (20)}$$

Since we impose no conditions on $\psi(x)$, k can assume any value so also energy E. i.e., for a free particle energy is not quantised. The solution of the equation 19 can also be written as

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

The time dependent wave function is

$$\underline{\Psi}(x, t) = \psi(x)e^{-i\omega t}$$

$$\underline{\Psi}(x, t) = Ae^{i(kx-\omega t)} + Be^{-i(kx-\omega t)}$$

The first term on the R.H.S represents a wave moving from left to right with amplitude A and the second term represents a wave moving from right to left with amplitude B. Suppose our particle is moving along the positive x direction (left to right) then B must be zero.

Thus $\underline{\Psi}(x, t) = Ae^{i(kx-\omega t)}$

$\therefore$ $$P(x) = |\underline{\Psi}(x, t)|^2 = |\psi(x)|^2 = |A|^2$$

It shows that probability density is constant, meaning the particles are equally likely to be found anywhere along the x-axis. This is in agreement with our old discussion that a free particles wave extending from $-\infty$ to ∞.

Infinite potential energy well
(Particle in a box - one dimension)

Here we solve the Schrodinger equation for a particle bouncing back and forth between the walls of a box. This problem is very much analogous to waves in a stretched string.

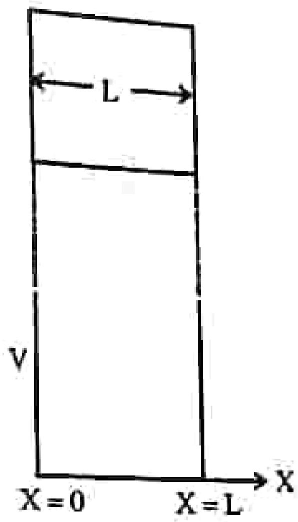


Figure 4.10

Consider a particle in a box whose motion is restricted along the x-axis between $x = 0$ and $x = L$. We assume that the particle does not lose energy when it collides with the walls of the box. (i.e., the total energy of the particle is constant). The potential energy of particle V is infinite on both sides of the box, while V is constant on the inside. Since the particle cannot have an infinite amount of energy it cannot exist outside the box so its wave function is zero for $x \leq 0$ and $x \geq L$. Our aim is to find ψ within the box i.e., between $x = 0$ and $x = L$.

Within the box the Schrodinger equation becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0$$

Take $V = 0$ the above equation becomes

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \text{ where } k^2 = \frac{2mE}{\hbar^2} \qquad \text{..... (1)}$$

The general solution of the equation is

$$\psi = A\cos kx + B\sin kx \qquad \text{..... (2)}$$

where A and B are constants to be evaluated. This is done by applying boundary conditions.

i.e., $\quad \psi = 0$ for $x = 0$ and $x = L$

Applying the first boundary condition i.e., $\psi = 0$, at $x = 0$ equation (2) becomes

$$0 = A\cos 0 + B\sin 0 \quad \text{i.e., } A = 0$$

$\therefore$ The wave function becomes

$$\psi = B\sin kx$$

Now applying the second boundary condition. i.e., $\psi = 0$ at $x = L$

$0 = B \sin kL$ ..... (3)

This happens only when $kL = n\pi$

where $n = 1, 2, \cdots$

Substituting for k in equation (3) we get

$$\frac{2mEL^2}{\hbar^2} = n^2\pi^2$$

$$E = \frac{n^2\hbar^2\pi^2}{2mL^2} = \frac{n^2h^2}{8mL^2}$$

This show that the energy of the particle can have only certain values. These values are

$$E_n = \frac{n^2h^2}{8mL^2} \quad ..... (4)$$

The integer n corresponding to the energy level E_n is called its quantum number. A particle confined to a box cannot have an arbitrary energy but only discrete values. This means that the energy levels are quantised.

Note : It may also be noted that the lowest possible energy of the particle corresponds to $n = 1$, we call this as the ground state of the particle.

$\therefore$ ground state energy $E_1 = \dfrac{h^2}{8mL^2}$

The particle in a one dimensional box-Wave function

The wave function of a particle in a box is $\psi = B \sin kx$ where $k = \dfrac{n\pi}{L}$

i.e., $\psi_n = B \sin \dfrac{n\pi}{L} x$ ..... (5)

This wave function satisfies all the conditions i.e., ψ_n is single valued function of x, and ψ_n and $\dfrac{d\psi_n}{dx}$ are continuous. Normalising the wave function we get

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n dx = \int_0^L B^2 \sin^2 \frac{n\pi x}{L} dx = \frac{B^2L}{2}$$

When the wave function is normalised.

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n dx = 1$$

i.e., $\dfrac{B^2L}{2} = 1$ or $B = \sqrt{2/L}$

The normalised wave functions of the particle are

$$\psi_n = \sqrt{2/L} \sin \frac{n\pi x}{L} \quad \text{with } n = 1, 2, 3, \cdots$$

The normalised wave functions ψ_1, ψ_2 and the corresponding probability densities are plotted.

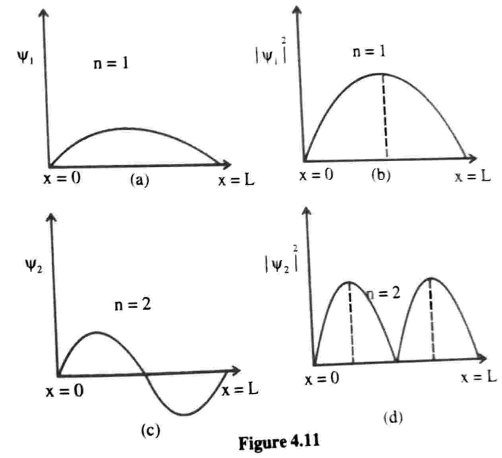


Figure 4.11

In every case $\psi_n^2 = 0$ at $x = 0$ and $x = L$ i.e., the probability of finding the particle at the two boundaries is zero. At any other point in the box the probability of finding the particle may be different fox different quantum numbers. For example $n = 1$, the maximum probability is at the middle of the box. When $n = 2$, the probability at the middle of the box is zero. But classical physics predicts the same probability at all points in the box which is equal to $\frac{1}{L}$.

Note : The ground state wave function corresponds to $n=1$ i.e., $\psi_1 = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$.

Example 12

Find the expectation value $\langle x\rangle$ of the position of a particle trapped in a box.

Solution

We have $\langle x\rangle = \int_{-\infty}^{\infty} \psi^* x\psi\, dx$

where $\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$

So $\langle x\rangle = \int_0^L x\frac{2}{L}\sin^2\frac{n\pi x}{L}dx$

or
$$\langle x\rangle = \frac{2}{L}\int_0^L x\sin^2\frac{n\pi x}{L}dx$$

$$\langle x\rangle = \frac{2}{L}\int_0^L x\left(\frac{1-\cos\frac{2n\pi x}{L}}{2}\right)dx$$

$$\langle x\rangle = \frac{1}{L}\left[\int_0^L x dx - \int_0^L x\cos\frac{2n\pi x}{L}dx\right]$$

$$\langle x\rangle = \frac{1}{L}\left[\frac{x^2}{2}\Bigg|_0^L - \left(\frac{x\sin\frac{2n\pi x}{L}}{\frac{2n\pi}{L}}\Bigg|_0^L - \int_0^L\frac{\sin\frac{2n\pi x}{L}dx}{\frac{2n\pi}{L}}\right)\right]$$

The second term vanishes for the limits.

$$\therefore \quad \langle x\rangle = \frac{1}{L}\left[\frac{L^2}{2} + \frac{\cos\frac{2n\pi x}{L}}{\left(\frac{2n\pi}{L}\right)^2}\Bigg|_0^L\right]$$

$$\langle x\rangle = \frac{1}{L}\left[\frac{L^2}{2} + \frac{\cos\frac{2n\pi}{L}\cdot L - \cos 0}{\left(\frac{2n\pi}{L}\right)^2}\right]$$

$$\langle x\rangle = \frac{1}{L}\left[\frac{L^2}{2} + \frac{1-1}{\left(\frac{2n\pi}{L}\right)^2}\right] = \frac{L}{2}.$$

i.e., The average position of the particle is always at the middle of the box for all values of the quantum numbers.

Example 13

Find the expectation value $\langle x^2\rangle$ of the position of the particle trapped in a box.

Solution

We have $\langle x^2\rangle = \int_{-\infty}^{\infty} \psi^* x^2\psi\, dx$

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

$$\therefore \quad \langle x^2\rangle = \int_0^L x^2\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}dx$$

$$\langle x^2\rangle = \frac{2}{L}\int_0^L x^2\sin^2\frac{n\pi x}{L}dx$$

$$\langle x^2\rangle = \frac{1}{L}\int_0^L x^2\left(1-\cos\frac{2n\pi x}{L}\right)dx$$

$$\langle x^2\rangle = \frac{1}{L}\left[\int_0^L x^2dx - \int_0^L x^2\cos\frac{2n\pi x}{L}dx\right] \quad \text{..... (1)}$$

$$\int_0^L x^2dx = \frac{2}{L}\left[\frac{x^3}{3}\right]_0^L = \frac{L^3}{3} \quad \text{..... (2)}$$

$$\int_0^L x^2\cos\frac{2n\pi}{L}xdx = x^2\frac{\sin\frac{2\pi nx}{L}}{\frac{2\pi n}{L}}\Bigg|_0^L - \int_0^L 2x\frac{\sin\frac{2\pi nx}{L}}{\frac{2\pi n}{L}}dx$$

when applying the limits first term vanishes.

$$\therefore \quad \int_0^L x^2\cos\frac{2n\pi x}{L}dx = -\frac{L}{\pi n}\int_0^L x\sin\frac{2n\pi x}{L}dx$$

$$= -\frac{L}{\pi n}\left[-x\frac{\cos\frac{2n\pi x}{L}}{\frac{2n\pi}{L}}\Bigg|_0^L - \int_0^L -\frac{\cos\frac{2\pi nx}{L}}{\frac{2\pi n}{L}}dx\right]$$

$$= -\frac{L}{\pi n}\left[-L\cdot\frac{1}{\frac{2n\pi}{L}} + \frac{\sin\frac{2\pi nx}{L}}{\frac{2\pi n}{L}}\Bigg|_0^L\right]$$

$$= -\frac{L}{\pi n}\left[-\frac{L^2}{2n\pi}+0\right]$$

$$= \frac{L^3}{2n^2\pi^2} \quad \text{..... (3)}$$

Substituting the values of the integrals from eq 2 and eq 3 in eq (1), we get

$$\langle x^2\rangle = \frac{1}{L}\left[\frac{L^3}{3} - \frac{L^3}{2n^2\pi^2}\right]$$

$$\langle x^2\rangle = \frac{1}{3}L^2 - \frac{L^2}{2n^2\pi^2}$$

Example 14

Show that $\Delta x\Delta p_x = \frac{h}{2}\sqrt{\frac{n^2}{12}-\frac{1}{2\pi^2}}$ for a particle in an infinite potential well.

Solution

$$\Delta x = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

From example 13, we have

$$\langle x^2\rangle = \frac{L^2}{3} - \frac{L^2}{2n\pi^2}$$

From example 12, we have

$$\langle x\rangle = \frac{L}{2}$$

$$\therefore \quad \langle x\rangle^2 = \frac{L^2}{4}$$

$$\therefore \quad \Delta x = \sqrt{\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \frac{L^2}{4}}$$

$$\Delta x = L\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}} \quad \text{..... (1)}$$

Similarly

Using $\Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2}$

$$\Delta p_x = \frac{nh}{2L}$$

$$\therefore \quad \Delta x\,\Delta p_x = \frac{nh}{2}\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}$$

or $$\Delta x\,\Delta p_x = \frac{h}{2}\sqrt{\frac{n^2}{12} - \frac{1}{2\pi^2}}$$

Example 15

A particle is in an infinite well is in the ground state with an energy of 1.26eV. How much energy must be added to the particle to reach the second excited state n = 3? The third excited state n = 4?

Solution

We have $E_n = \dfrac{n^2h^2}{8mL^2}$

For the ground state $n = 1$

$$E_1 = \frac{h^2}{8mL^2} = 1.26\text{eV given}$$

$$E_3 = \frac{9h^2}{8mL^2} = 9\times 1.26\text{eV}$$

$\therefore$ Energy to be added, $\Delta E = E_3 - E_1 = 8\times 1.26\text{eV}$

$= 10.08\text{eV}$.

For $n = 4$ $E_4 = 16\dfrac{h^2}{8mL^2} = 16\times 1.26\text{eV}$

Now $\Delta E = E_4 - E_1 = 15\times 1.26 = 18.9\text{eV}$

Example 16

A particle is trapped in an infinite one dimensional well of width L. If the particle is in its ground state, evaluate the probability to find the particle between x = 0 and $x = \frac{1}{3}$.

Solution

Probability $P = \int_{x_1}^{x_2} |\psi(x)|^2\,dx$

Here $\psi_1(x) = \sqrt{\dfrac{2}{L}}\sin\dfrac{\pi x}{L}$ since n = 1

$$P\left(0,\frac{L}{3}\right) = \int_0^{L/3}\frac{2}{L}\sin^2\frac{\pi x}{L}dx = \frac{2}{L}\int_0^{L/3}\left(\frac{1-\cos\frac{2\pi x}{L}}{2}\right)dx$$

$$= \frac{1}{L}\int_0^{L/3}\left(1-\cos\frac{2\pi x}{L}\right)dx$$

$$P\left(0,\frac{L}{3}\right) = \frac{1}{L}\left[x - \sin\frac{2\pi x}{L}\cdot\frac{L}{2\pi}\right]_0^{L/3}$$

$$P\left(0,\frac{L}{3}\right) = \frac{1}{L}\left[\frac{L}{3} - \sin\frac{2\pi}{3}\cdot\frac{L}{2\pi}\right]$$

$$P\left(0,\frac{L}{3}\right) = \frac{1}{L}\left[\frac{L}{3} - \frac{\sqrt{3}}{2}\cdot\frac{L}{2\pi}\right]$$

$$P = \frac{1}{3} - \frac{\sqrt{3}}{4\pi} = 0.1954$$

Particle in a box-two dimensions

Here we extend the problem of particle in a box - one dimension to two dimensions. We can see that the principal features of solution of one dimensional problem remains the same, but a new important feature called degeneracy will come in to play. This is very important in our study of atomic physics.

Consider a particle moves freely in a two dimensional region $0 < x < L$ and $0 < y < L$ but encounters infinite barriers beyond the regions. Such a two dimensional infinite potential well is mathematically represented by

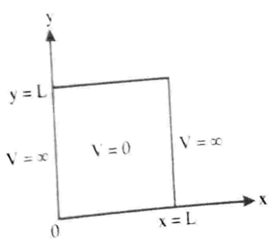


Figure 4.12

$V = 0, \quad 0 \le x < L, \quad 0 \le y < L$

$V = \infty$ otherwise

Since potential energy is a function of both x and y, wave function also depends on x and y.

The Schrödinger equation in two dimensions can be written as

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2 \psi(x, y)}{\partial x^2} + \frac{\partial^2 \psi(x, y)}{\partial y^2}\right) = E\psi(x, y)$$

or $$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{2mE}{\hbar^2}\psi = 0 \qquad \text{..... (21)}$$

We want to solve this second order partial differential equation.

The solution of the Schrodinger equation is $\psi(x, y)$. We assume that $\psi(x, y)$ can be written as the product of one function that depends only on x and another that depends only on y.

i.e., $$\psi(x, y) = f(x)\, g(y) \qquad \text{..... (22)}$$

$$\frac{\partial \psi}{\partial x} = f'(x) g(y)$$

$$\frac{\partial^2 \psi}{\partial x^2} = f''(x) g(y) \qquad \text{..... (23)}$$

$$\frac{\partial \psi}{\partial y} = f(x) g'(y)$$

$$\frac{\partial^2 \psi}{\partial y^2} = f(x) g''(y) \qquad \text{..... (24)}$$

Substituting eqs 22, 23 and 24 in eq 21, we get

$$f''(x) g(y) + f(x) g''(y) + \frac{2mE}{\hbar^2} f(x) f(y) = 0$$

Dividing throughout the equation by $f(x) g(y)$, we get.

$$\frac{f''(x)}{f(x)} + \frac{g''(y)}{g(y)} + \frac{2mE}{\hbar^2} = 0 \qquad \text{..... (25)}$$

Since the coordinates x and y are independent, the terms containing x will not cancel with terms containing y. For this to happen each term must be a constant.

$$\frac{f''(x)}{f(x)} = -\frac{g''(y)}{g(y)} - \frac{2mE}{\hbar^2} = -\alpha^2 \text{(say)} \qquad \text{..... (26)}$$

or $$\frac{f''(x)}{f(x)} = -\alpha^2$$

$$f''(x) = -\alpha^2 f(x)$$

or $$\frac{d^2 f(x)}{dx^2} = -\alpha^2 f(x) \qquad \text{..... (27)}$$

From eq 26, we have

$$\frac{g''y}{g(y)} = \alpha^2 - \frac{2mE}{\hbar^2} = -\beta^2 \text{(say)} \qquad \text{..... (28)}$$

or $$\frac{g''y}{g(y)} = -\beta^2$$

$$\frac{d^2 g(y)}{dy^2} = -\beta^2 g(y) \qquad \text{..... (29)}$$

From eq 28, we have

$$\alpha^2 + \beta^2 = \frac{2mE}{\hbar^2} \qquad \text{..... (30)}$$

The solutions of eqs 27 and 29 are

$$f(x) = A_1 \sin \alpha x + B_1 \cos \alpha x \qquad \text{..... (31)}$$

and $$g(y) = A_2 \sin \beta y + B_2 \cos \beta y \qquad \text{..... (32)}$$

Where A_1, B_1, A_2 and B_2 are constants to be determined. The values of these constants can be obtained by applying the boundary conditions. We know that ψ vanishes at the surface of infinite potential.

$\psi = 0$ when $x = 0$ and also at $x = L$. The condition on x effects only on $f(x)$.

i.e., $f(x) = 0$ when $x = 0$ and $x = L$.

Applying these conditions to eq 31, we get

$$f(x) = A_1 \sin \alpha x + B_1 \cos \alpha x$$

At $x = 0$ $\quad 0 = 0 + B_1 \Rightarrow B_1 = 0$

$$\therefore \quad f(x) = A_1 \sin \alpha x \qquad \text{..... (35)}$$

Now apply the second condition

$$f(x) = 0 \text{ at } x = L$$

we get $0 = A_1 \sin \alpha L$

or $\sin \alpha L = 0$

But we know that

$$\sin n_x \pi = 0 \text{ for } n_x = 1, 2, 3, \ldots$$

comparing we get

$$\alpha L = n_x \pi$$

or
$$\alpha = \frac{n_x \pi}{L}$$

$\therefore$ Our solution $f(x)$ (see eq 35) becomes

$$f(x) = A_1 \sin \frac{n_x \pi x}{L} \qquad \text{..... (36)}$$

Similarly we apply boundary condition on $g(y)$

i.e., $g(y) = 0$ when $y = 0$ and $y = L$

Proceeding as before

$$g(y) = A_2 \sin \frac{n_y \pi y}{L} \quad \text{where} \quad \frac{n_y \pi}{L} = \beta$$

$\therefore$ The complete solution of the Schrödinger equation (21) is

$$\psi(x, y) = f(x)\, g(y)$$

$$\psi(x, y) = A_1 A_2 \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \qquad \text{..... (37)}$$

The constant $A_1 A_2$ can be determined by the normalisation of $\psi(x, y)$

i.e.,
$$\iint |\psi(x, y)|^2\, dx\, dy = 1$$

$$\int_0^L \int_0^L A_1^2 A_2^2 \sin^2 \frac{n_x \pi x}{L} \sin^2 \frac{n_y \pi y}{L}\, dx\, dy = 1$$

$$A_1^2 A_2^2 \int_0^L \sin^2 \frac{n_x \pi x}{L} dx \int_0^L \sin^2 \frac{n_y \pi y}{L}\, dy = 1$$

$$A_1^2 A_2^2 \int_0^L \left(\frac{1 - \cos \frac{2n_x \pi x}{L}}{2} \right) dx \int_0^L \left(\frac{1 - \cos \frac{n_y \pi y}{L}}{2} \right) dy = 1$$

$$\frac{A_1^2 A_2^2}{4} \left(x - \sin \frac{2n_x \pi x}{L} \cdot \frac{L}{2n_x \pi} \right)_0^L \left(y - \sin \frac{2n_y \pi y}{L} \cdot \frac{L}{2n_y \pi} \right)_0^L = 1$$

$$\frac{A_1^2 A_2^2}{4} L^2 = 1$$

$$\therefore \quad A_1 A_2 = \frac{2}{L}$$

$$\therefore \quad \psi(x, y) = \frac{2}{L} \sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \qquad \text{..... (38)}$$

Finally we determine the energy eigen values. Substituting the value of α and β in eq 30, we get

$$\left(\frac{n_x \pi}{L} \right)^2 + \left(\frac{n_y \pi}{L} \right)^2 = \frac{2mE}{\hbar^2}$$

or
$$\frac{\pi^2}{L^2} (n_x^2 + n_y^2) = \frac{2mE}{\hbar^2}$$

$$\therefore \quad E = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} (n_x^2 + n_y^2)$$

Put $\hbar = \frac{h}{2\pi}$

$$E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2)$$

This is the expression for energy eigen values of a particle in a two dimensional infinite potential well. Since E depends on the values of n_x and n_y it is usually written as

$$E_{n_x, n_y} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2) \quad \text{..... (39)}$$

Equation 39 shows that energy levels are quantised as n_x and n_y are integers.

Energy eigen values of the particle

The energy eigen value of the particle is

$$E_{n_x, n_y} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2)$$

The wave functions are

$$\psi_{n_x, n_y}(x, y) = \frac{2}{L}\sin\frac{n_x \pi x}{L}\sin\frac{n_y \pi y}{L}$$

The integers n_x and n_y are called quantum numbers which are required to describe the stationary state of the particle.

For the ground state $n_x = 1, n_y = 1$

The ground state wave function is

$$\psi_{1,1}(x, y) = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}$$

and the energy associated with the ground state is called as zero point energy is given by

$$E_{1,1} = \frac{h^2}{8mL^2}(1^2 + 1^2) = \frac{2h^2}{8mL^2}$$

For the first excited state we have two possibilities

n_x	n_y
1	2
2	1

so
$$\psi_{1,2}(x, y) = \frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}$$

$$\psi_{2,1}(x, y) = \frac{2}{L}\sin\frac{2\pi x}{L}\sin\frac{2\pi y}{L}$$

The corresponding eigen values are

$$E_{1,2} = \frac{h^2}{8mL^2}(1^2 + 2^2) = \frac{5h^2}{8mL^2}$$

$$E_{2,1} = \frac{h^2}{8mL^2}(2^2 + 1^2) = \frac{5h^2}{8mL^2}$$

This shows that for different quantum numbers

$$(n_x = 1, n_y = 2 \text{ or } (n_x = 2, n_y = 1)$$

We get different wave functions but having same energy eigen value. This is called degeneracy and the energy levels are said to be degenerate

Degeneracy

The property that two or more quantum states of a particle with different sets of quantum numbers and different wave functions having the same value of energy is called degeneracy.

When we extend our problem to three dimensions the effects of degeneracy become more significant. In the case of atomic physics the degeneracy is a major contributor to the structure and properties of atoms.

Example 17

A particle is confined to a two dimensional box of length L and width L. The energy eigen values are

$$E = \frac{h^2}{8mL^2}\left(n_x^2 + \frac{n_y^2}{4}\right).$$ Find the two lowest energy levels.

Solution

$$E_{n_x,n_y} = \frac{h^2}{8mL^2}\left(n_x^2 + \frac{n_y^2}{4}\right)$$

For $n_x = 1$ and $n_y = 1$, we get the lowest one

$$E_{1,1} = \frac{h^2}{8mL^2}\left(1^2 + \frac{1^2}{4}\right) = 1.25\frac{h^2}{8mL^2}$$

For $n_x = 1$ and $n_y = 2$, we get the next higher energy level

$$\therefore \quad E_{1,2} = \frac{h^2}{8mL^2}\left(1^2 + \frac{2^2}{4}\right) = \frac{2h^2}{8mL^2}$$

Example 18

What is the next level above $E = 50\frac{h^2}{8mL^2}$ of the two dimensional particle in a box in which the degeneracy is greater than two?

Solution

We have $E_{n_x,n_y} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2)$

But it is given that $E_{n_x,n_y} = \frac{h^2}{8mL^2}\cdot 50$

Comparing we get $n_x^2 + n_y^2 = 50$

This gives us $n_x = 5$ and $n_y = 5$

The degeneracy of the state is one

To get next levels we try for

$$n_x^2 + n_y^2 > 50$$

The different possibilities are

n_x	n_y	E_{n_x,n_y} in terms of $\frac{h^2}{8mL^2}$
6	4	52
4	6	52
7	2	53
2	7	53
7	3	58
3	1	58
6	5	61
5	6	61
7	4	65
4	7	65
8	1	65
1	8	65

The levels (7, 4), (4, 7), (8, 1) and (1, 8) having same energy and the degeneracy is 4 fold.

Simple harmonic oscillator

The one dimensional motion of a point mass about a fixed point under a force is called a linear harmonic oscillator. The study of this is one of the most fundamental problems in classical physics. Since it serves as a good approximate model for many problems in classical and quantum mechanics. For example the theory of radiation, the quantisation of lattice vibrations, the vibrations of diatomic and polyatomic molecules etc. can be readily approximated as similar to the motion of a harmonic oscillator.

Classical theory of harmonic oscillator

Consider a particle of mass m moves to and fro about a point along a line (one dimension). Let x be the displacement of the particle from the mean position. The force (restoring) acting on the particle at that instant is given by

$$F = -kx \qquad \text{..... (39)}$$

where k is called the force constant. -ve sign shows that the restoring force acting on the particle is always opposite to its displacement.

Since $F = m\frac{d^2x}{dt^2}$, the classical equation of motion of the harmonic oscillator is

$$m\frac{d^2x}{dt^2} = -kx$$

or $$\frac{d^2x}{dt^2} = \frac{-k}{m}x$$

Put $\frac{k}{m} = \omega^2$, where ω is the regular frequency

or $$\frac{d^2x}{dt^2} = -\omega^2 x \qquad \text{..... (40)}$$

solving this equation, the general solution is

$$x = a\sin(\omega t + \phi) \qquad \text{..... (41)}$$

where a is the amplitude and ϕ is the initial phase of the particle.

The time period T of the motion is given by

$$T = \frac{2\pi}{\omega} = 2\pi\sqrt{\frac{m}{k}} \qquad \text{..... (42)}$$

$\therefore$ The frequency $$\upsilon = \frac{1}{T} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad \text{..... (43)}$$

Now the energy of the harmonic oscillator can be easily found.

The potential energy, V is given by

$$V = \int_0^V dV = \int_0^x \frac{dV}{dx}dx = -\int_0^x (F)dx \quad (\because\ F = -\frac{dV}{dx})$$

or $$V = \int_0^x +kx\,dx \quad (\because\ F = -kx)$$

$$V = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2 \quad (\because\ \omega^2 = \frac{k}{m}) \qquad \text{..... (44)}$$

The kinetic energy K is given by

$$K = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2$$

$$K = \frac{1}{2}m\left[\frac{d}{dt}\{a\sin(\omega t + \phi)\}\right]^2$$

$$K = \frac{1}{2}m\,a^2\omega^2\cos^2(\omega t + \phi)$$

$$K = \frac{1}{2}m\,a^2\omega^2\left(1 - \sin^2(\omega t + \phi)\right)$$

$$K = \frac{1}{2}m\,a^2\omega^2\left(1 - \frac{x^2}{a^2}\right) = \frac{1}{2}m\,\omega^2(a^2 - x^2) \qquad \text{..... (45)}$$

$\therefore$ The total energy of the harmonic oscillator is

$$E = K + V = \frac{1}{2}m\,\omega^2(a^2 - x^2) + \frac{1}{2}m\omega^2x^2$$

$$E = \frac{1}{2}m\omega^2a^2 \qquad \text{..... (46)}$$

The classical probability of finding the particle executing harmonic motion within a small distance dx.

Probability is defined as the ratio of the time which the particle takes to pass over a distance dx during the course of its one oscillation to the period of oscillation $\left(T = \frac{2\pi}{\omega}\right)$.

If the particle passes through the distance dx in one direction in time dt, then the probability P(x) dx of finding it within dx is given by

$$P(x)\,dx = \frac{2dt}{T} = \frac{2dt}{\frac{2\pi}{\omega}} = \frac{\omega}{\pi}dt \qquad \text{..... (47)}$$

Using $x = a\sin(\omega t + \phi)$

$dx = a\omega\cos(\omega t + \phi)dt$

$$dx = a\omega\sqrt{1-\frac{x^2}{a^2}}\,dt = \omega\sqrt{a^2-x^2}\,dt$$

or
$$dt = \frac{dx}{\omega\sqrt{a^2-x^2}}$$

$$\therefore\ P(x)dx = \frac{dx}{\pi\sqrt{a^2-x^2}}$$

From eq. 46 $a^2 = \dfrac{2E}{m\omega^2}$

$$\therefore\quad P(x)\,dx = \frac{dx}{\pi\sqrt{\dfrac{2E}{m\omega^2}-x^2}} \qquad \text{..... (48)}$$

$\therefore$ Probability density function turns out to be

$$P(x) = \frac{1}{\pi\sqrt{\dfrac{2E}{m\omega^2}-x^2}} \qquad \text{..... (49)}$$

This formula shows that when $x \to \pm a$ $P(x) \to \infty$ also $P(x) = \dfrac{1}{\pi a}$ at $x = 0$. This is its minimum value. The classical probability distribution curve is shown below:

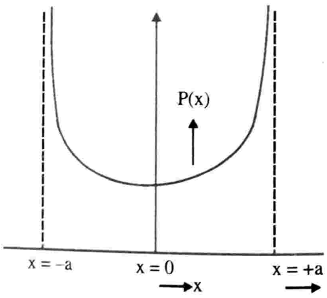


Figure 4.13

Quantum mechanical theory of harmonic oscillator

Here we shall analyse the motion of the harmonic oscillator from the point of view of the quantum mechanics.

We know that the time independent one dimensional Schrodinger equation of a particle moving along the x-axis is

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi(x) = 0$$

For the harmonic oscillator, the potential energy V is given by

$$V = \frac{1}{2}m\omega^2x^2$$

$\therefore$ The schrodinger equation for the one dimensional harmonic oscillator is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}m\omega^2x^2\right)\psi = 0 \qquad \text{..... (50)}$$

This is a second order equation with variable coefficient. Therefore to solve this equation we have to transform this equation into a standard form whose solution is known.

We introduce a new independent variable

$y = \alpha x$, where α is a constant.

$$\therefore\quad \frac{d\psi}{dx} = \frac{d\psi}{dy}\cdot\frac{dy}{dx} = \frac{d\psi}{dy}\alpha$$

$$\frac{d^2\psi}{dx^2} = \frac{d}{dx}\left(\frac{d\psi}{dx}\right) = \frac{d}{dx}\left(\frac{\alpha\psi}{dy}\right) = \alpha\frac{d}{dx}\left(\frac{d\psi}{dy}\right)$$

$$\frac{d^2\psi}{dx^2} = \alpha\frac{d}{dy}\left(\frac{d\psi}{dy}\right)\cdot\frac{dy}{dx} = \alpha\frac{d}{dy}\left(\frac{d\psi}{dy}\right)\cdot\alpha$$

$$\frac{d^2\psi}{dx^2} = \alpha^2\frac{d^2\psi}{dy^2}$$

Now eqn. 50 becomes

$$\alpha^2\frac{d^2\psi}{dy^2}+\frac{2m}{\hbar^2}\left(E-\frac{1}{2}\frac{m\omega^2y^2}{\alpha^2}\right)\psi=0$$

or

$$\frac{d^2\psi}{dy^2}+\left(\frac{2mE}{\hbar^2\alpha^2}-\frac{m^2\omega^2y^2}{\hbar^2\alpha^4}\right)\psi=0 \quad \text{..... (51)}$$

Let us choose $\frac{m^2\omega^2}{\hbar^2\alpha^4}=1$ and $\frac{2mE}{\hbar^2\alpha^2}=\lambda$

$$\therefore \quad \alpha^4=\frac{m^2\omega^2}{\hbar^2}$$

or

$$\alpha^2=\frac{m\omega}{\hbar}$$

$$\therefore \quad \lambda=\frac{2mE}{\hbar^2\alpha^2}=\frac{2mE}{\hbar^2\frac{m\omega}{\hbar}}=\frac{2E}{\hbar\omega} \quad \text{..... (52)}$$

$\therefore$ Eqn. 51 becomes

$$\frac{d^2\psi}{dy^2}+(\lambda-y^2)\psi=0 \quad \text{..... (53)}$$

Solving this equation and the solution is subjected to the admissibility conditions of ψ i.e. $\psi\to 0$ when $y\to\pm\infty$ we can see that we get an acceptable solution only when

$$\lambda=2n+1 \text{ with } n=0,1,2,.... \quad \text{..... (54)}$$

Using this in eqn. 52, we get the energy levels of harmonic oscillator.

$$\lambda=\frac{2E}{\hbar\omega}$$

or

$$(2n+1)=\frac{2E_n}{\hbar\omega}$$

or

$$E_n=\frac{(2n+1)\hbar\omega}{2}=\left(n+\frac{1}{2}\right)\hbar\omega$$

$$E_n=\left(n+\frac{1}{2}\right)\frac{h}{2\pi}.2\pi\upsilon$$

or

$$E_n=\left(n+\frac{1}{2}\right)h\upsilon \text{ with } n=0,1,2,3 \quad \text{..... (55)}$$

This shows that the energy levels are quantised in steps of $h\upsilon$.

When n = 0, we get the lowest energy of the harmonic oscillator.

i.e.

$$E_0=\frac{1}{2}h\upsilon \quad \text{..... (56)}$$

This value is called the zero point energy. The energy levels of harmonic oscillator is given below. It may also be noted that the all adjacent energy levels are equispaced with a separation of $h\upsilon$.

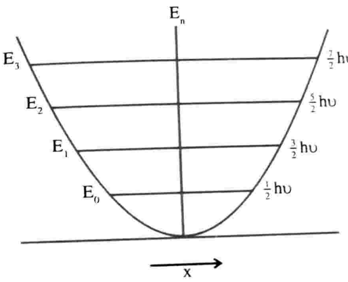


Figure 4.14

Note: For the solution of eq. 53 see appendix D.

Harmonic oscillator wave functions

When we solved the equation

$$\frac{d^2\psi}{dy^2}+(\lambda-y^2)\psi=0 \text{ we could see that}$$

$$\lambda=2n+1 \text{ with } n=0,1,2,3....$$

This shows that for each value of n we get an acceptable wave function. So we have n waves functions. Therefore in general the solution (see appendix B) is found to be

$$\psi_n = \left(\frac{\alpha}{\pi^{1/2}2^n n!}\right)^{1/2} H_n(y)e^{-y^2/2} \quad \ldots\ldots (57)$$

where $\alpha = \sqrt{\frac{m\omega}{\hbar}}$ and $H_n(y)$ is called Hermite polynomial.

The first term of the eqn. 57 on the R.H.S is the normalisation constant and $H_n(y)e^{-y^2/2}$ is the wave function. Some values of Hermite polynomials are given below:

n	$H_n(y)$	$\lambda_n = 2n+1$	E_n
0	1	1	$\frac{1}{2}h\upsilon$
1	$2y$	3	$\frac{3}{2}h\upsilon$
2	$4y^2-2$	5	$\frac{5}{2}h\upsilon$
3	$8y^3-12y$	7	$\frac{7}{2}h\upsilon$
4	$16y^4-48y^2+12$	9	$\frac{9}{2}h\upsilon$

When $n=0$, the corresponding wave function is

$$\psi_0(y) = \left(\frac{\alpha}{\pi^{\frac{1}{2}}2^n n!}\right)^{\frac{1}{2}} H_0(y)e^{-\frac{y^2}{2}}$$

$$\psi_0 = \left(\frac{\alpha}{\pi^{\frac{1}{2}}}\right)^{\frac{1}{2}} e^{-\frac{y^2}{2}}$$

Put $y = \alpha x$

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{\frac{1}{2}}}\right)^{\frac{1}{2}} e^{-\frac{\alpha^2 x^2}{2}} \quad \ldots\ldots (58)$$

The wave function $\psi_0(x)$ and the probability distribution function $|\psi_0(x)|^2$ as a function of x are given below.

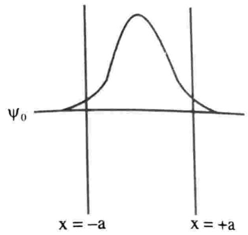


Figure 4.15(a)

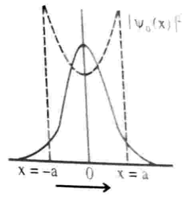


Figure 4.15 (b)

The dashed line in the second figure gives the classical probability distribution. It shows that the quantum mechanical oscillator and the classical oscillator behave exactly in the opposite manner.

The next five wave functions ψ_1, ψ_2, ψ_3, ψ_4 and ψ_5 are depicted as shown below.

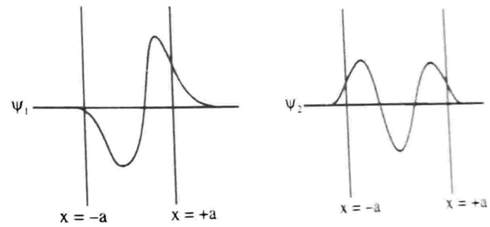


Figure 4.16

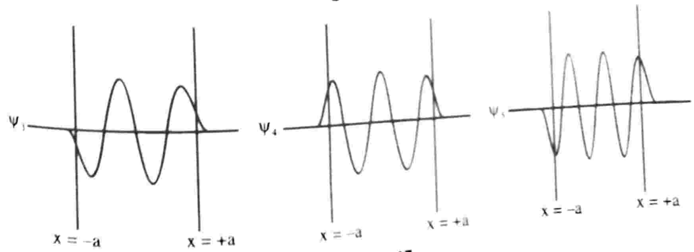


Figure 4.17

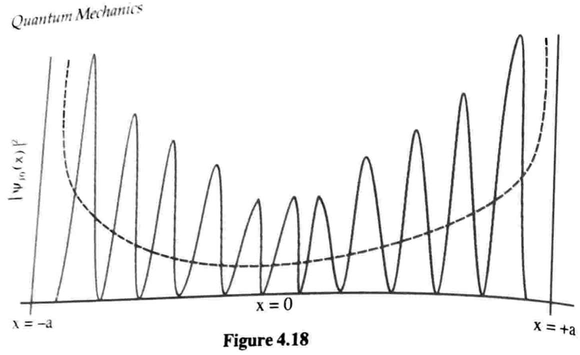


Figure 4.18

When the value n increases the classical curve is seen to agree with the average behaviour of quantum mechanical curve. See the figure drawn for n = 10. The dashed line curve represents the probability function for the classical harmonic oscillator. This is again an illustration of the correspondence principle which states that classical prediction and quantum prediction are one and the same for large value of n.

Example 19

Find the zero point energy in electron volt of a pendulum whose period is 1s.

Solution

We have zero point energy,

$$E_0 = \frac{1}{2}h\upsilon = \frac{h}{2T} = \frac{h}{2} \qquad (\because T = 1s)$$

$$E_0 = \frac{6.62\times10^{-34}}{2} = 3.31\times10^{-34}J$$

$$E_0 = \frac{3.31\times10^{-34}}{1.6\times10^{-19}}eV = 2.07\times10^{-15}eV.$$

Example 20

Find the expectation value of potential energy of linear harmonic oscillator where the wave function is $\left(\frac{m\omega^2}{\pi\hbar}\right)^{\frac{1}{4}} e^{\frac{-m\omega x^2}{2\hbar}}$

Given that $\int_0^\infty t^{\frac{1}{2}}e^{-t}dt = \frac{\sqrt{\pi}}{2}$

Solution

We have $\langle V\rangle = \int_{-\infty}^{\infty} V|\psi|^2\,dx$

Potential energy $V = \frac{1}{2}m\omega^2x^2$

$$\therefore \quad \langle V\rangle = \frac{1}{2}m\omega^2\int_{-\infty}^{\infty} x^2\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{2}} e^{-\frac{m\omega x^2}{\hbar}}dx$$

$$\langle V\rangle = \frac{m\omega^2(m\omega)^{\frac{1}{2}}}{2(\pi\hbar)^{\frac{1}{2}}}\int_{-\infty}^{\infty} x^2 e^{-\frac{m\omega x^2}{\hbar}}dx$$

$$\langle V\rangle = \frac{m^{\frac{3}{2}}\omega^{\frac{5}{2}}}{\pi^{\frac{1}{2}}\hbar^{\frac{1}{2}}}\int_0^\infty x^2 e^{-\frac{m\omega x^2}{\hbar}}dx \qquad \text{....(1)}$$

Put $\frac{m\omega}{\hbar}x^2 = t \qquad \frac{m\omega}{\hbar}2x\,dx = dt$

$$\therefore \quad dx = \frac{\hbar}{m\omega}\frac{dt}{2x}$$

or $$dx = \frac{\hbar}{m\omega}\cdot\frac{1}{2}\frac{dt}{\hbar^{\frac{1}{2}}}\frac{(m\omega)^{\frac{1}{2}}}{t^{\frac{1}{2}}}$$

$$dx = \frac{\hbar^{\frac{1}{2}}}{2(m\omega)^{\frac{1}{2}}}\frac{dt}{t^{\frac{1}{2}}}$$

Now eqn (1) becomes

$$\langle V\rangle = \frac{m^{\frac{3}{2}}\omega^{\frac{5}{2}}}{\pi^{\frac{1}{2}}\hbar^{\frac{1}{2}}}\int_0^\infty \frac{\hbar}{m\omega}t\,e^{-t}\frac{dt\,\hbar^{\frac{1}{2}}}{2(m\omega)^{\frac{1}{2}}t^{\frac{1}{2}}}$$

$$\langle V \rangle = \frac{\hbar\omega}{2\pi^{\frac{1}{2}}} \int_0^\infty t^{\frac{1}{2}} e^{-t} dt$$

Using $\int_0^\infty t^{\frac{1}{2}} e^{-t} dt = \frac{\sqrt{\pi}}{2}$

$$\therefore \quad \langle V \rangle = \frac{\hbar\omega}{2\pi^{\frac{1}{2}}} \cdot \frac{\pi^{\frac{1}{2}}}{2} = \frac{1}{4}\hbar\omega$$

$$\langle V \rangle = \frac{1}{4}\frac{h}{2\pi} \cdot 2\pi\upsilon = \frac{1}{4}h\upsilon$$

Example 21

The ground state energy of an oscillating electron is 124 eV. How much energy must be added to the electron to move it to the second excited state? The fourth excited state?

Solution

We have $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$

For the ground state $n = 0$

$$E_1 = \frac{1}{2}\hbar\omega = 1.24\text{eV}$$

For the second excited state $n = 2$

$$E_2 = \frac{5}{2}\hbar\omega = 5 \times 1.24 = 6.2\text{eV}$$

$\therefore$ Energy to be added, $\Delta E = E_2 - E_1 = 6.2 - 1.24 = 4.96\text{eV}$

For the fourth excited state $n = 4$

$$E_4 = \frac{9}{2}\hbar\omega = 9 \times 1.24 = 11.16\text{eV}$$

$\therefore$ Energy to be added, $\Delta E = E_4 - E_1 = 11.16 - 1.24 = 9.92\text{eV}$

Example 22

At the classical turning points $\pm a$ of the simple harmonic oscillator $K = 0$, $E = V$. From this relationship show that $a = \left(\frac{\hbar\omega}{k}\right)^{\frac{1}{2}}$ for an oscillator in its ground state. Find the turning points in the first and second excited states?

Solution

For a harmonic oscillator

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega = K + V$$

For the ground state $(n = 1)$ classical turning point $K = 0$, thus

$$\frac{1}{2}\hbar\omega = V$$

$$\frac{1}{2}\hbar\omega = \frac{1}{2}ka^2$$

$$\therefore \quad a = \pm\sqrt{\frac{\hbar\omega}{k}}$$

For the second excited state $n = 2$

$$\therefore \quad \frac{5}{2}\hbar\omega = \frac{1}{2}ka^2$$

$$a = \pm\sqrt{\frac{5\hbar\omega}{k}}$$

Potential energy steps

So far we were dealing with quantum particles which are confined to certain regions and found that the energy levels are quantised. Here we consider a particle moving in a region of constant potential energy suddenly moves into a region of another constant potential energy. We can say that the particle encounters a potential energy step. Our aim here is to solve Schrodinger equation of this particle to get the wave function and its properties. Since the particle is not confined its energy levels are not quantised. We have to consider two cases one is the total energy (E) of the particle is greater than the potential energy (V) step the other one is E < V

Case I $E > V_0$

Consider a particle of energy E moving towards a potential energy step of height V_0 with $E > V_0$ along x-direction. Mathematically potential step is written as

$$V(x) = 0 \quad \text{for } x < 0$$
$$= V_0 \quad \text{for } x > 0$$

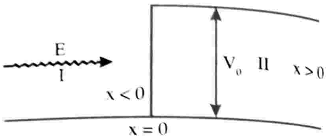


Figure 4.19

The motion of the particle is schematically represented in figure 4.19. The particle moves through two regions I and II.

Schrodinger equation of the particle in region I $(x < 0)$ is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_I(x)}{dx^2} = E\psi_I$$

or

$$\frac{d^2\psi_I(x)}{dx^2} = \frac{-2mE}{\hbar^2}\psi_I(x)$$

put

$$\frac{2mE}{\hbar^2} = k_I^2$$

$$\frac{d^2\psi_I(x)}{dx^2} = -k_I^2\psi_I(x) \qquad \text{..... (60)}$$

The solution of this equation is

$$\psi_I(x) = Ae^{ik_Ix} + Be^{-ik_Ix} \qquad \text{..... (61)}$$

Similarly the Schrodinger equation of the particle in region II $(x > 0)$ is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_{II}(x)}{dx^2} + V_0\psi_{II}(x) = E\psi_{II}(x)$$

or

$$\frac{d^2\psi_{II}(x)}{dx^2} = \frac{-2m}{\hbar^2}(E - V_0)\psi_{II}(x)$$

put

$$\frac{2m}{\hbar^2}(E - V_0) = k_2^2$$

Thus

$$\frac{d^2\psi_{II}(x)}{dx^2} = -k_2^2\psi_{II}(x) \qquad \text{..... (62)}$$

The solution of this equation is

$$\psi_{II}(x) = Ce^{ik_2x} + De^{-ik_2x} \qquad \text{..... (63)}$$

The coefficients A, B, C and D in equations 61 and 63 can be determined by applying boundary conditions on $\psi_I(x)$ and $\psi_{II}(x)$ (For this see example 23).

i.e.,

$$(\psi_I(x))_{x=0} = (\psi_{II}(x))_{x=0}$$

and

$$\left(\frac{d\psi_I(x)}{dx}\right)_{x=0} = \left(\frac{d\psi_{II}}{dx}\right)_{x=0}$$

The time dependent wave functions $\psi_I(x)$ and $\psi_{II}(x)$ are

$$\psi_I(x, t) = Ae^{i(k_1x-\omega t)} + Be^{-i(k_1x+\omega t)} \qquad \text{..... (64)}$$

$$\psi_{II}(x, t) = Ce^{i(k_2x-\omega t)} + De^{-i(k_2x+\omega t)} \qquad \text{..... (65)}$$

In eq 64, the first term represents a wave moving from left to right i.e., it represents the incident wave with amplitude A The second term is a wave moving from right to left i.e., it represents the reflected wave into region I with amplitude B. From A and B we can very well calculate the reflection coefficient (R). It is also called as reflection probability. Reflection probability defined as the ratio between reflected beam intensity and the incident beam intensity.

i.e., $$R = \frac{\text{Reflected beam intensity}}{\text{Incident bean intensity}}$$

Since intensity α (amplitude)^2

we have $$R = \frac{|B|^2}{|A|^2} \qquad \text{..... (66)}$$

Modulus comes because usually amplitudes are complex quantities.

In eq 65, the first term is a wave travelling from left to right i.e., it represents the transmitted wave with amplitude C in the region. The second term is wave travelling from right to lect. But in the second region there is no barrier to have a reflected wave. So we can very well assume that $D = 0$. From the coefficients A and C we can calculate the transmission coefficient (I). It is also called as transmission probability. Transmission probability is defined as the ratio between the transmitted beam intensity to the incident beam intensity.

$$\text{i.e., } T = \frac{\text{Transmitted beam intensity}}{\text{Incident bean intensity}}$$

$$\text{i.e., } T = \frac{|C|^2}{|A|^2} \qquad \text{..... (67)}$$

Potential energy steps $E < V_0$

In region $I(x < a)$, the Schrodinger equation is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_I(x)}{dx^2} = E\psi_I(x) \qquad x < 0$$

or

$$\frac{d^2\psi_I(x)}{dx^2} = \frac{-2mE}{\hbar^2}\psi_I(x)$$

put

$$\frac{2mE}{\hbar^2} = k_I^2$$

$\therefore$

$$\frac{d^2\psi_I(x)}{dx^2} = -k^2\psi_I(x) \qquad \text{..... (68)}$$

The solution is

$$\psi_I(x) = Ae^{ik_Ix} + Be^{-ik_Ix} \qquad \text{..... (69)}$$

In region II $(x > a)$, the Schrodinger equation is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi_{II}(x)}{dx^2} + V_0\psi_{II} = E\psi_{II}$$

or

$$\frac{d^2\psi_{II}(x)}{dx^2} = \frac{2m}{\hbar^2}(V_0 - E)\psi_{II}(x)$$

put

$$\frac{2m}{\hbar^2}(V_0 - E) = k_2^2$$

$$\frac{d^2\psi_{II}(x)}{dx^2} = k_2^2\psi_{II}(x) \qquad \text{..... (70)}$$

The solution of this equation is

$$\psi_{II}(x) = Ce^{k_2x} + De^{-k_2x} \qquad \text{..... (71)}$$

when $x \to \infty$, the wave function in the region must vanish. For this to satisfy C must be zero.

$$\text{i.e., } \quad \psi_{II}(x) = De^{-k_2x} \text{ for } x > 0 \qquad \text{..... (72)}$$

Since $E < V_0$, the region II is classically forbidden region to the particle. But eq 72 shows that the probability of finding the particle in the region II is non zero. This shows that the particle is penetrated into the classically forbidden region. The probability density in the region II is $|\psi_{II}(x)|^2$

From eq 72, we get

$$|\psi_{II}(x)|^2 \propto e^{-2k_2x}$$

$$P(x) \propto e^{-2k_2x} \qquad \text{..... (73)}$$

Penetration distance (Δx)

It is defined as the distance, travelled by the particle, over which the probability drops by $\frac{1}{e}$.

$$\text{That is } \frac{P(x)}{e} \propto e^{-2k_2(x+\Delta x)} \qquad \text{..... (74)}$$

$$\frac{\text{eq 74}}{\text{eq 73}} \text{ gives } \quad \frac{1}{e} = e^{-2k_2\Delta x}$$

or

$$e^{-1} = e^{-2k_2\Delta x}$$

or

$$2k_2\Delta x = 1$$

i.e.,

$$\Delta x = \frac{1}{2k_2}$$

$$\Delta x = \frac{\hbar}{2\sqrt{2m(V_0 - E)}} \quad \because k_2 = \sqrt{\frac{2m}{\hbar^2}(V_0 - E)} \qquad \text{..... (75)}$$

This shows that in order to get over the potential energy step or enertering the region II $(x > 0)$, the particle must gain some energy of at least $V_0 - E$. This is against law of conservation of energy. However this penetration is permitted by the uncertainty principle without violating conservation of energy. According to uncertainty relationship $\Delta E \Delta t \sim \hbar$. The conservation of energy does not apply at times smaller than Δt. The particle borrows an amount of energy ΔE and returns the borrowed energy within a time $\Delta t \sim \frac{\hbar}{\Delta E}$. In this way the statusquo of law of conservation of energy is maintained.

Suppose the particle borrows some energy such that the particle moves in the region II.

$\therefore$ The borrowed energy = $V_0 - E + K$, $V_0 - E$ is the energy required by the particle just to reach the top of the potential step and K is the kinetic energy required by the particle to move. This energy must be returned within a time Δt given by the uncertainty relationship.

i.e.,
$$\Delta t \simeq \frac{\hbar}{\Delta E}$$

$$\Delta t \simeq \frac{\hbar}{V_0 - E + K} \qquad \text{..... (76)}$$

The speed of the particle can be determined from

$$K = \frac{1}{2} m v^2$$

or
$$v = \sqrt{\frac{2K}{m}} \qquad \text{..... (77)}$$

$\therefore$ The distance of penetration

$$\Delta x = \frac{v \Delta t}{2} \qquad \text{..... (78)}$$

The factor $\frac{1}{2}$ comes because in time Δt the particle travels a distance Δx in the forbidden region and return through the same distance to get back to the allowed region I.

Substituting eqs 76 and 77 in eq 78, we get

$$\Delta x = \frac{1}{2} \sqrt{\frac{2K}{m}} \frac{\hbar}{V_0 - E + K} \qquad \text{..... (79)}$$

The distance travelled depends upon K only all others being constants. To find the maximum distance travelled by the particle, we differentiate Δx with respect to K and put equal to zero.

$$\frac{d}{dK} \Delta x = -\frac{1}{2} \sqrt{\frac{2K}{m}} \frac{\hbar}{(V_0 - E + K)^2} + \frac{\hbar}{V_0 - E + K} \frac{1}{\sqrt{2m}} \frac{-1}{2\sqrt{K}}$$

Putting $\frac{d}{dK} \Delta x = 0$, we get

$$\frac{1}{2} \sqrt{\frac{2K}{m}} \frac{\hbar}{(V_0 - E + K)^2} = \frac{\hbar}{(V_0 - E + K)} \frac{1}{\sqrt{2m}} \frac{1}{2\sqrt{K}}$$

i.e.,
$$\sqrt{\frac{2K}{m}} \cdot \frac{\hbar}{V_0 - E + K} = \frac{1}{\sqrt{2m}} \frac{1}{\sqrt{K}}$$

or
$$2K = V_0 - E + K$$

i.e.,
$$K = V_0 - E \qquad \text{..... (80)}$$

Putting this value in eq 79, we get $(\Delta x)_{max}$

$$(\Delta x)_{max} = \frac{1}{2} \frac{\sqrt{2(V_0 - E)}}{\sqrt{m}} \frac{\hbar}{2(V_0 - E)}$$

$$(\Delta x)_{max} = \frac{1}{2} \frac{\hbar}{\sqrt{2m(V_0 - E)}} \qquad \text{..... (81)}$$

This is the same expression (75) that we already obtained by solving Schrodinger equation. This shows that the penetration into the forbidden region given by the solution to the Schrodinger equation is consistent with the uncertainty relationship.

Potential energy barrier

When a particle approaches a region in which its potential energy is greater than its total initial energy, the particle is said to approach a barrier potential. It is referred to as a barrier because the particle's presence in this region demands its potential energy to be in excess of its initial total energy.

Let a particle of energy E approach a barrier of height V. If E > V, we expect the particle to be totally transmitted across the barrier. For E < V, the classical prediction is one of total reflection (see the figure below)

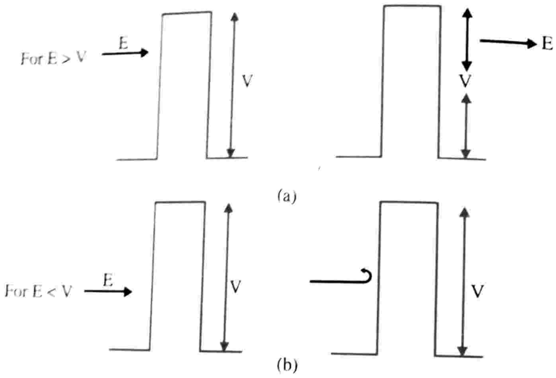


Figure 4.20

Quantum mechanical analysis of the problem of barrier potential - The tunnel effect

When we solve the barrier potential problem quantum mechanically (writing the appropriate Schrodinger equations and solving them to obtain the physically acceptable wave functions), we can see that even for E < V the particle can tunnel through the barrier region as well as go on to the other side of the barrier. This implies that even for E < V, the particle can some how manage to tunnel through the barrier which is classically forbidden. This is referred

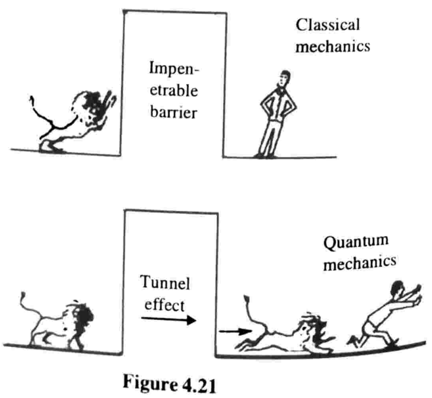


Figure 4.21

to as the tunnelling effect. This is only a quantum mechanical phenomenon which has no classical counter part. Alpha decay by radioactive elements, the field emission of electrons from a cold metal surface, the switching action of a tunnel diode, the reverse break down of semiconductor diodes, insulation breakdown of electric insulator are some of the phenomena which could be explained on the basis of tunnel effect.

Tunnel effect

Consider a particle of mass m and energy E is incident from the left on a barrier of height V and wide L. We assume that E < V and V = 0 on either side of the barrier. V = 0 on either side implies that, it is field free region. i.e. no forces act on the particle in these regions. The barrier potential is described by the equations.

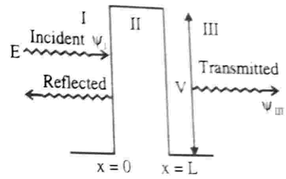


Figure 4.22

$V = 0$ for $-\infty \le x \le 0$ (Region I)

$V = V$ for $0 \le x \le L$ (Region II)

$V = 0$ for $L \le x \le \infty$ (Region III)

The time independent Schrodinger equation for the three regions are

For region I, $$\frac{d^2\psi_I}{dx^2} + \frac{2mE}{\hbar^2}\psi_I = 0 \qquad \text{.....(82)}$$

For region II, $$\frac{d^2\psi_{II}}{dx^2} - \frac{2m}{\hbar^2}(V-E)\psi_{II} = 0 \qquad \text{.....(83)}$$

For region III, $$\frac{d^2\psi_{III}}{dx^2} + \frac{2mE}{\hbar^2}\psi_{III} = 0 \qquad \text{.....(84)}$$

Put $$\frac{2mE}{\hbar^2} = k_1^2 \qquad \text{.....(85)}$$

and $$\frac{2m(V-E)}{\hbar^2} = k^2 \qquad \text{.....(86)}$$

Now equations 82, 83and 84 take the form

$$\frac{d^2\psi_1}{dx^2} + k_1^2\psi_1 = 0 \qquad \text{.....(87)}$$

$$\frac{d^2\psi_{II}}{dx^2} - k^2\psi_{II} = 0 \qquad ..... (88)$$

$$\frac{d^2\psi_{III}}{dx^2} + k_I^2\psi_{III} = 0 \qquad ..... (89)$$

The solutions corresponding to ψ_I, ψ_{II} and ψ_{III} are, therefore

$$\psi_I(x) = Ae^{ik_Ix} + Be^{-ik_Ix} \qquad ..... (90)$$

$$\psi_{II}(x) = Ce^{kx} + De^{-kx} \qquad ..... (91)$$

$$\psi_{III}(x) = Fe^{ik_Ix} + Ge^{-ik_Ix}$$

When these solutions are combined with the time dependent part of the wave function, we realise that the first term in ψ_I represents a wave travelling from left to right ie. the incident wave. The second term here represents a wave travelling from right to left i.e. the reflected wave. The same interpretation holds for the first and the second terms in the solution for ψ_{III}. But, since there is no reflecting boundary in region III, there can be no reflected wave in that region. Therefore, we must have

$$G = 0$$

and $$\psi_{III} = Fe^{ik_Ix} \qquad ..... (92)$$

Reflection and transmission coefficients

The coefficients A in ψ_I and B in ψ_I and F in ψ_{III} are the amplitudes of the incident, reflected and transmitted waves respectively. Since intensity of the beam is proportional to absolute square of the amplitude, we have

Incident beam intensity $\alpha\ |A|^2 = A^*A$, Reflected been intensity $\alpha\ |B|^2 = B^*B$

and transmitted beam intensity $\alpha\ |F|^2 = F^*F$

$$\frac{\text{Reflected beam intensity}}{\text{Incident beam intensity}} = \frac{|B|^2}{|A|^2} = \frac{B^*B}{A^*A}.$$

The ratio between reflected beam intensity and the incident beam intensity is called the reflection coefficient or reflection probability and is denoted by R.

$$\therefore \quad \frac{\text{Transmitted beam intensity}}{\text{Incident beam intensity}} = \frac{|F|^2}{|A|^2} = \frac{F^*F}{A^*A}$$

The ratio on the L.H.S. is called the transmission coefficient transmission probability and is denoted by T.

i.e. $$T = \frac{F^*F}{A^*A} \qquad ..... (98)$$

It can be easily shown that

$$R + T = 1$$

By applying the appropriate boundary conditions on ψ_I, ψ_{II} and ψ_{III} we can evaluate the transmission probability T and is found to be

$$T \approx e^{-2kL} \qquad ..... (99)$$

where $$k = \sqrt{\frac{2m(V-E)}{\hbar^2}}$$

This shows that the transmission probability is determined by kL. When kL is large transmission probability is low. If E << V, k will be large so T will be small. If L is large again T will be small.

The above discussion shows that a quantum mechanical particle can tunnel through potential barriers which is classically forbidden. The tunnel effect is observed in various atomic and nuclear phenomena. For example an alpha particle whose kinetic energy is only a few MeV is able to escape from a nucleus whose potential well is nearly 25 MeV high. This is called alpha decay.

Note : The derivation of transmission probability is found in appendix C.

Another example of quantum tunnelling is Ammonia inversion. The structure ammonia molecule is trigonal pyramidal shape as shown in figure below. If we try to move the nitrogen atom along the axis of the molecule towards the plane of the hydrogen atoms, repulsion will be caused by hydrogen atoms which produces potential energy of the form shown in figure below.

Unless we give sufficient energy to nitrogen atom, it should not be able to surmount the barrier and appear on the other side of the plane of hydrogens. Quantum mechanics predicts that nitrogen can tunnel through the barrier and appear on the other side of the plane. It has been experimentally verified that nitrogen atom tunnels back and forth with a frequency in excess of 10^{10} oscillations per second which is in perfect agreement with the prediction of quantum mechanics.

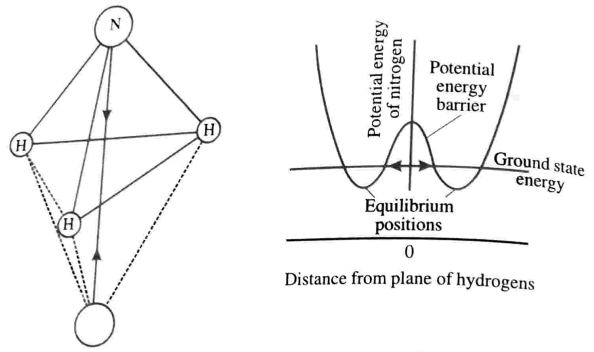


Figure 4.23: Structure of Ammonia molecule

Finally we discuss the scanning tunneling microscope which works on the principle of quantum tunneling.

Tunneling microscope

The *scanning tunneling microscope* (STM) *is a type of electron microscope that is used for viewing surfaces at the atomic level and three dimensional images of a sample.*

The STM was invented by Gerd Bining and Heinrich Rohrer (at Zurich) who shared the 1986 Nobel Prize with Ernst Ruska, the inventor of the electron microscope. A good STM having 0.1 nm lateral resolution and 0.01 nm depth resolution. It can be used not only on ultra high vacuum but also in air and various other liquids or gases and at temperature ranging from near zero kelvin, to a few hundred degree celsius.

The STM is based on the concept of quantum tunneling, which is the ability of electrons to tunnel through a potential barrier.

Principle of STM

When a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them. The resulting tunneling current is a function of tip position, applied voltage, and the local density of states of the sample. Information is acquired by monitoring the current as the probe's position scans across the surface and is usually displayed in image form.

An STM consists of mainly 5 parts. They are

(i) Scanning tip (Probe)

The tip is often made of tungsten or platinum-iridium. Tungsten tips are usually made by electrochemical etching and platinum iridium tips by mechanical shearing.

(ii) Piezo electric tube

This is to control the position of the tip. The thickness of certain ceramics changes when a voltage is applied across them, a property called piezoelectricity. The changes might be several tenths of a nanometer per volt. In an STM, the piezo electric tube controls the movement of the scanning tip (probe) in x and y directions across a surface and in the z direction perpendicular to the surface.

(iii) Coarse sample to tip control

This is the mechanism through which the separation between the tip and the sample can be precisely adjusted.

(iv) Vibration isolation system

It is due to extreme sensitivity of tunnel current to height, proper vibration isolation is essential for obtaining usable results. A mechanical spring or gas spring system is often used to keep the STM free from vibrations.

(v) Computer

Maintaining the tip position with respect to the sample, scanning the sample and acquiring the data is computer controlled. The computer may also be used for enhancing the image with the help of image processing as well as performing quantitative measurements.

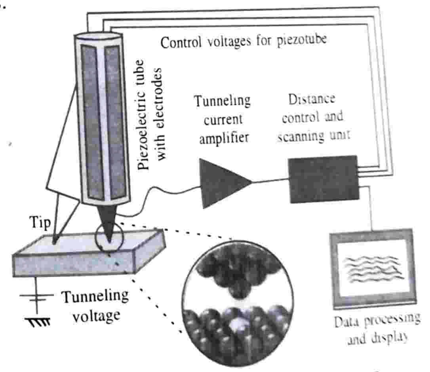


Figure 4.24: Schematic view of an STM

Working

Firstly a voltage bias is applied and the scanning tip is brought close to the sample by means of coarse sample to tip control. Fine control of the tip in all three directions when near the sample is typically piezo electric.

In this situation the voltage bias will cause electrons to tunnel between the tip and the sample, creating a current that can be measured. Once tunneling is established, the tips bias and position with respect to the sample can be varied and data is obtained from the resulting changes in current. If the tip is moved across the sample in the x-y plane, the changes in surface height and density of states changes in current. These changes are mapped in images.

Uses of STM

(i) To obtain atomic scale images of metal surfaces.

(ii) It provides a three dimensional profile of the surface which is very useful for characterising surface roughness, observing surface defects and determining the size and confirmation of molecules and aggregates on the surface.

(iii) Another use of STM is the atomic deposition of metals (Au, Ag etc.) with any desired pattern.

(iv) STM tip can use to rotate the individual bonds within single molecules. The electrical resistance of the molecule depends on the orientation of the bond, so the molecule effectively becomes a molecular switch.

Example 23

For particles with energy $E > V_0$ incident on the potential energy step use ψ_I and ψ_2 and evaluate the constants A, B and C by applying the boundary conditions at x = 0 also find reflection and transmission probability.

Solution

We have $\psi_I(x) = Ae^{ik_1x} + Be^{-ik_1x}$

and $\psi_{II}(x) = Ce^{-ik_2x}$

Applying the boundary condition

$$(\psi_I(x))_{x=0} = (\psi_{II}(x))_{x=0}$$

i.e.,
$$A + B = C \qquad \text{..... (1)}$$

Applying the second boundary condition

$$\left(\frac{d\psi_I(x)}{dx}\right)_{x=0} = \left(\frac{d\psi_{II}(x)}{dx}\right)_{x=0}$$

$$ik_1A - ik_1B = ik_2C$$

or
$$k_1A - k_1B = k_2C \qquad \text{..... (2)}$$

Multiply eq(1) with k_1 and add to eq (2), we get

$$2k_1A = (k_1 + k_2)C$$

$$\therefore \quad C = \frac{2k_1A}{k_1 + k_2} \qquad \text{..... (3)}$$

From eq (1), we have

$$B = C - A = \frac{2k_1A}{k_1 + k_2} - A$$

$$\therefore \quad B = \frac{(k_1 - k_2)}{(k_1 + k_2)}A \qquad \text{..... (4)}$$

$$\text{Reflection probability} = \frac{|B|^2}{|A|^2} = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2}$$

$$\text{Transmission probability} = \frac{|C|^2}{|A|^2} = \frac{4k_1^2}{(k_1 + k_2)^2}$$

Example 24

A beam of electrons of energy 4eV hits on a potential barrier of height 5eV and width 1A. What is the transmission probability of electrons.

Solution

$$E = 4eV = 4 \times 1.6 \times 10^{-19} J$$

$$V = 5eV = 5 \times 1.6 \times 10^{-19} J$$

$$m = 9 \times 1.10^{-31} kg \text{ and } \hbar = 1.054 \times 10^{-34} J.s.$$

using
$$k = \sqrt{\frac{2m(V - E)}{\hbar^2}} = \frac{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19}}}{1.054 \times 10^{-34}}$$

$$k = 5.12 \times 10^9 m^{-1}$$

$\therefore$ The transmission probability

$$T = e^{-2kL}$$

$$T = e^{-2\times5.12\times10^{9}\times10^{-10}} \qquad (\because L = 1\text{Å} = 10^{-10}\,\text{m})$$

$$T = e^{-1.024}$$

$$T = 0.359$$

Example 25

A beam of electrons is incident on a barrier 6eV and 0.1nm wide. Find the energy they should have if 10 percent of them are to get through the barrier.

Solution

$$V = 6\text{eV} = 6\times1.6\times10^{-19}\,\text{J} = 9.6\times10^{-19}\,\text{J}$$

$$L = 0.1\text{nm} = 0.1\times10^{-9}\,\text{m}$$

$$T = \frac{10}{100} = 0.1$$

Using $T = e^{-2kL}$

$$0.1 = e^{-k\times0.2\times10^{-9}}$$

$\therefore$ $\ln(0.1) = -k\times2\times10^{-10}$

or $k = \dfrac{-\ln(0.1)}{2\times10^{-10}} = \dfrac{\ln 10}{2\times10^{-10}} = 1.15\times10^{10}$

Using $k^2 = \dfrac{2m(V-E)}{\hbar^2}$

we get $\dfrac{k^2\hbar^2}{2m} = V - E$

or $E = V - \dfrac{k^2\hbar^2}{2m}$

$$E = 9.6\times10^{-19} - \frac{(1.15\times10^{+10})^2\times(1.054\times10^{-34})^2}{2\times9.1\times10^{-31}}$$

$$E = 9.6\times10^{-19} - 8.07245\times10^{-19}$$

$$E = 1.53\times10^{-19}\,\text{J}$$

or $E = \dfrac{1.53\times10^{-19}}{1.6\times10^{-19}} = 0.956\,\text{eV}$

IMPORTANT FORMULAE

1. Probability density $\psi^*(x)\psi(x) = |\psi(x)|^2$
2. Time independent Schrödinger equation

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi \quad \text{in one dimension}$$

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2\psi(x,y)}{\partial x^2} + \frac{\partial^2\psi(x,y)}{\partial y^2}\right] + V(x,y)\psi(x,y) = E\psi(x,y) \quad \text{in two dimensions}$$

$$\frac{-\hbar^2}{2m}\nabla^2\psi(\bar{r}) + V(r)\psi(\bar{r}) = E\psi(\bar{r}) \quad \text{in three dimensions}$$

3. Relation between time dependent and independent wave functions

$$\underline{\psi}(x,t) = \psi(x)e^{-i\frac{E}{\hbar}t} = \psi(x)e^{-i\omega t}$$

4. Boundary conditions on wave function

$$(\psi_I(x))_{x=0} = (\psi_{II}(x))_{x=0}$$

$$\left(\frac{d\psi_I(x)}{dx}\right)_{x=0} = \left(\frac{d\psi_{II}(x)}{dx}\right)_{x=0}$$

5. Normalisation condition

$$\int_{-\infty}^{\infty}\psi^*(x)\psi(x)\,dx = 1$$

6. Probability in the interval x_1 to x_2

$$\int_{x_1}^{x_2}\psi^*(x)\psi(x)\,dx$$

7. Mean or expectation value of any dynamical variable $f(x)$

$$\langle f(x)\rangle = \int_{-\infty}^{\infty}\psi^*(x)f(x)\psi(x)\,dx$$

8. Particle in a box (Infinite potential energy well)

$$V(x) = 0 \qquad 0 < x < L$$

$$= \infty \qquad \text{otherwise}$$

Wave function $\psi_n = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$, $n = 1, 2, 3, \ldots$

The energy eigen values $E_n = \frac{n^2h^2}{8mL^2}$, $n = 1, 2, 3, \ldots$

9. Free particle

Wave function $\psi(x, t) = Ae^{i(kx-\omega t)}$

Energy $E = \frac{\hbar^2 k^2}{2m}$

10. Particle in two dimensional box

$$V(x, y) = 0 \qquad 0 \le x \le L, \quad 0 \le y \le L$$
$$= \infty \qquad \text{otherwise}$$

Wave function $\psi_{n_x, n_y}(x, y) = \frac{2}{L}\sin\frac{n_x \pi x}{L}\sin\frac{n_y \pi y}{L}$

Energy eigen values $E_{n_x, n_y} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2)$

11. The classical probability of finding the particle executing S.H.M. is

$$P(x)dx = \frac{dx}{\pi\sqrt{a^2 - x^2}}.$$

12. Schrodinger equation for one dimensional harmonic oscillator

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \frac{1}{2}m\omega^2x^2\psi(x) = E\psi(x)$$

13. Harmonic oscillator wave function

$$\psi_n(x) = \left(\frac{\alpha}{\pi^{1/2}2^n n!}\right)^{1/2} H_n(\alpha x)e^{\frac{-\alpha^2x^2}{2}}, \ \alpha = \sqrt{\frac{m\omega}{\hbar}}$$

Ground state wave function

$$\psi_0(x) = \left(\frac{\alpha}{\pi^{1/2}}\right)^{1/2} e^{\frac{-\alpha^2x^2}{2}}$$

14. The energy levels of harmonic oscillator

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \ n = 0, 1, 2, \ldots$$

Ground state energy $E_0 = \frac{1}{2}\hbar\omega.$

15. Potential energy step

$$V(x) = 0 \qquad \text{for } x < 0$$
$$= V_0 \qquad \text{for } x > 0$$

For $E > V_0$

$$\psi_I(x) = Ae^{ik_1x} + Be^{-ik_1x}$$
$$\psi_{II}(x) = Ce^{ik_2x}$$

For $E < V_0$

$$\psi_I(x) = Ae^{ik_1x} + Be^{-ik_1x}$$
$$\psi_{II}(x) = De^{-k_2x}$$

Probability density in the classically forbidden region II

$$P(x) \propto e^{-2k_2x}$$

16. Penetration distance (Δx)

$$\Delta x = \frac{\hbar}{2\sqrt{2m(V_0 - E)}}$$

17. Potential energy barrier

$$V(x) = 0 \qquad -\infty \le x \le 0$$
$$= V \qquad 0 \le x \le L$$
$$= 0 \qquad L \le x \le \infty$$

$$\psi_I(x) = Ae^{ik_1x} + Be^{-ik_1x}$$
$$\psi_{II}(x) = Ce^{kx} + De^{-kx}$$
$$\psi_{III}(x) = Fe^{ik_1x}$$

18. Reflection probability $= \frac{|B|^2}{|A|^2}$

19. Transmission probability $= \frac{|F|^2}{|A|^2}$

20. Transmission probability of tunnel effect

$$T \simeq e^{-2kL}, \ k = \sqrt{\frac{2m(V - E)}{\hbar^2}}$$

UNIVERSITY MODEL QUESTIONS

Section A

(Answer questions in about **two** *or* **three** *sentences)*

Short answer type questions

1. Distinguish between Newton's second law and Schrödinger equation.
2. What is wave function?
3. What is an evanescent wave?
4. Write down two properties shared by classical and quantum waves.
5. Electron can penetrate into forbidden region. Give justification.
6. Mention two properties that wave should obey while crossing the boundary.
7. Give the three properties of matter waves.
8. What is a free particle?
9. What is a confined particle?
10. Distinguish between free and confined particle.
11. What is Schrödinger equation and what is its solution?
12. Write down the Schrödinger in one dimension and explain the symbols used.
13. Give mathematical expression for probability amplitude, probability density and probability in terms of wave function.
14. What is meant by normalising a wave function?
15. What is meant by expectation value of a dynamical variable?
16. Write down the expressions for the expectation values of position and momentum.
17. What is a stationary state?
18. What are the two continuity conditions of the wave function?
19. What is a harmonic oscillator?
20. What is zero point energy of harmonic oscillator? Write down its expression.
21. What are similarities of the predictions of classical and quantum oscillators?
22. What are the dissimilarities of the predictions of classical and quantum oscillators?
23. Explain the correspondence principle on the basis of harmonic oscillator.
24. What are the predictions of quantum harmonic oscillator?
25. Define a potential energy step.
26. Define reflection probability.
27. Define transmission probability.
28. What is potential energy step penetration?
29. Define the penetration distance.

30. What is potential energy barrier?
31. What is tunnel effect?
32. Write down three phenomena which can be explained on the basis of tunnel effect.
33. What are the factors on which the transmission probability of tunnel effect depend?
34. What is scanning tunnelling microscope?
35. What is the principle of S.T.M?

Section B

(Answer questions in about half a page to one page)

Paragraph / Problem type questions

1. Explain the behaviour of light wave crossing a boundary.
2. Discuss the behaviour of surface waves at the boundary.
3. Explain the behaviour of matter waves at the boundary.
4. What are the properties of classical waves shared by matter waves?
5. What are the boundary conditions that have to be satisfied by matter waves?
6. Distinguish between a free particle and a confined particle.
7. Set up the Schrodinger equation using a simple matter wave.
8. Write down the procedures of solving Schrodinger equation.
9. Find the solutions of Schrödinger equation for constant potential energy.
10. Find the solutions of the Schrödinger equation for a free particle.
11. Find the energy eigen values of a free particle in two dimensional box.
12. Find the value of the normalisation constant A for the wave function $Axe^{-\frac{x^2}{2}}$.

    Given that $\int_0^\infty t^n e^{-t} dt = n!$ and $\left(\frac{1}{2}\right)! = \frac{\sqrt{\pi}}{2}$ $\left[\left(\frac{4}{\pi}\right)^{\frac{1}{4}}\right]$

13. The wave function of a certain particle is $\psi = A\cos^2 x$ for $-\frac{\pi}{2} < x < \frac{\pi}{2}$. Find the value of A. $\left[\sqrt{\frac{8}{3\pi}}\right]$
14. The ground state of the hydrogen atom is described by the wave function $\psi(r) = e^{-\frac{r}{a}}$ $\left[A = \frac{1}{\sqrt{\pi a^3}}\right]$

    Normalise it [0]

15. Calculate $\langle x \rangle$ for the wave function $e^{-x}\sin \alpha x$

16. Evaluate $\langle r \rangle$ when the wave function is $\psi(r)=\left(\frac{1}{\pi a^3}\right)^{\frac{1}{2}} e^{-\frac{r}{a}}$ $\left[\frac{3a}{2}\right]$

17. The linear harmonic oscillator wave function is given by $\psi(x)=\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}} e^{-\frac{m\omega}{2\hbar}x^2}$. What are the expectation values of position and momentum? [0, 0]

18. Find the probability that a particle in a box L wide can be found between $x=0$ and $x=\frac{L}{n}$ when it is in the n^{th} state $\left[\frac{1}{n}\right]$

19. A particle is in a cubic box with infinitely hard walls whose edges are L long. The wave functions of the particle are given by $\psi = A\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}$

$n_x = 1, 2, 3, \ldots, n_y = 1, 2, 3, \ldots,$ and $n_z = 1, 2, 3, \ldots,$ Normalise it $\left[\left(\frac{2}{L}\right)^{\frac{3}{2}}\right]$

20. A potential barrier of width $2Å$ and height $5eV$ is being approached by a beam of electrons of energy E. The transmission probability is found to be 0.5. What is the value of E? [4.89 eV]

21. Electrons with energies of $0.4eV$ are incident on a barrier $3eV$ high 0.1 nm wide. Find the approximate probability for these electrons to penetrate the barrier. [0.44]

22. Find the quantum mechanical probability of finding the oscillator in the classical limits ($-a$ to a). Take $\psi(x)=\left(\frac{\alpha}{\pi^{\frac{1}{2}}}\right)^{\frac{1}{2}} e^{-\frac{\alpha^2x^2}{2}}$, where $\alpha=\left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}}$ [84.3%]

23. A particle of mass m and energy E moving in the positive x-direction, encounters a ame dimensional potential barrier at $x=0$. The barrier is defined by

$V=0$ for $x<0$

$V=V_0$ for $x\geq 0$ (V_0 is positive and $E>V_0$)

If the wave function of the particle in the region $x<0$ is given as $Ae^{ikx}+Be^{-ikx}$

a) Find the ratio B/A

b) If $\frac{B}{A}=0.4$, find $\frac{B}{A}=0.4, \frac{E}{\chi_0}$ and the transmission and reflection coefficients.

(IIT – JAM 2005)

24. The wave function $\psi_n(x)$ of a particle confined to a one dimensional box of length L with rigid walls is given by

$$\psi_n(x)=\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L},\ n=1, 2, 3.....$$

a) Determine the energy eigenvalues. Also determine the eigenvalues and eigen functions of the momentum operator.

b) Show that the energy eigen functions are not the eigen functions of the momentum operator. (IIT – JAM 2008)

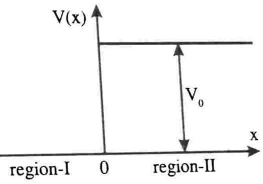
25. A particle of mass m is confined in a one dimensional box of unit length. At time $t=0$ the wave function of the particle is $\psi(x,0)=A\sin 2\pi x\cos\pi x$,

a) Write the wave function at later time t.

b) Find the expectation values of momentum and energy at $t=0$.

(IIT – JAM 2009)

26. A free particle of mass 'm' with energy $V_0/2$ is incident from left on a step potential of height V_0 as shown in the figure below.



Writing down the time independent Schrödinger equation in both the regions, obtain the corresponding general solutions. Apply the boundary conditions to find the wave functions in both the regions. Determine the reflection coefficient R. What is the transmission coefficient T? (IIT – JAM 2010)

27. A particle of mass m is placed in a 3 - D cubic box of side a. What is the degeneracy of its energy level with energy $14\left(\frac{\hbar^2\pi^2}{2ma^2}\right)$ [6]

(IIT – JAM 2016)

28. In a certain region of space a particle is described by the wave function $\psi(x)=Cxe^{-bx}$ where C and b are real constants. By substituting this into Schrödinger equation, find the potential energy in this region and also find the energy of the particle $\left[V(x)=\frac{-\hbar^2 b}{mx},\ E=\frac{-\hbar^2b^2}{2m}\right]$

Section C

*(Answer questions in about **two pages**)*

Long answer type questions (Essays)

1. Solve the Schrödinger equation of a particle in a one dimensional box and find out its energy.
2. Solve the Schrödinger equation of a particle in a two dimensional box and find out its energy.
3. Treat harmonic oscillator problem quantum mechanically. Arrive at energy eigen values and wave functions.
4. Discuss the quantum mechanical analysis of the problem of barrier potential and evaluate the transition probability.

Hints to problems

12. We have $\int_{-\infty}^{\infty} \psi\psi^* dx = 1$

$$|A|^2 \int_{-\infty}^{\infty} x^2 e^{-x^2} dx = 1$$

$$|A|^2 2\int_0^{\infty} x^2 e^{-x^2} dx = 1 \qquad \text{..... (1)}$$

Put $x^2 = t \therefore 2x\,dx = dt$ or $dx = \frac{dt}{2x}$

$$\therefore \quad dx = \frac{dt}{2t^{\frac{1}{2}}}$$

Now eqn (1) becomes

$$|A|^2 2\int_0^{\infty} \frac{t\,e^{-t}dt}{2t^{\frac{1}{2}}} = |A|^2 2\int_0^{\infty} t^{\frac{1}{2}}\, e^{-t}dt = 1$$

or $\quad |A|^2 \frac{\sqrt{\pi}}{2} = 1$

$$\therefore \quad |A| = \left(\frac{4}{\pi}\right)^{\frac{1}{4}}$$

13. $|A|^2 \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos^4 x\,dx = 1$ or $2|A|^2 \int_0^{\frac{\pi}{2}} \cos^4 x\,dx = 1$

$$\int_0^{\frac{\pi}{2}} \cos^4 x\,dx = \frac{3\pi}{16}$$

14. $\int \psi\psi^* d\tau = 1$

$$|A|^2 \int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} e^{-\frac{2r}{a}} r^2 \sin\theta\, d\theta d\phi$$

15. $\langle x \rangle = \int_{-\infty}^{\infty} x\psi^*\psi\, dx$

$$\langle x \rangle = |N|^2 \int_{-\infty}^{\infty} x e^{-2x} \sin^2 \alpha x\, dx = 0$$

Integrand is odd.

16. $\langle r \rangle = \int_{-\infty}^{\infty} r\psi\psi^* d\tau$

$$\langle r \rangle = \frac{1}{\pi a^3}\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} r\, e^{-\frac{2r}{a}} r^2 \sin\theta\, d\theta d\phi dr$$

$$\langle r \rangle = \frac{4\pi}{\pi a^3}\int_0^{\infty} r^3\, e^{-\frac{2r}{a}} dr = \frac{4}{a^3}\int_0^{\infty} r^3\, e^{-\frac{2r}{a}} dr$$

Put $\frac{2r}{a} = t$ and use $\int_0^{\infty} t^n e^{-t} dt = n!$

17. Try your self
18. Probability,

$$P = \int \psi^*(x)\psi(x) dx$$

$$P = \frac{2}{L}\int_0^{\frac{L}{n}} \sin^2 \frac{n\pi x}{L} dx\,, \quad \int_0^{\frac{L}{n}} \sin^2 \frac{n\pi x}{L} dx = \frac{L}{2n}$$

19. $\int \psi^* \psi \, d\tau = 1$

$$\int_0^L\int_0^L\int_0^L |A|^2 \sin^2\frac{n_x \pi x}{L} \sin^2\frac{n_y \pi y}{L} \sin^2\frac{n_z \pi z}{L}$$

But $\int_0^L \sin\frac{n_x \pi x}{L} dx = \frac{L}{2}$ similarly each integral.

20. See example 25

21. $T = e^{-2kL}$, $k = \sqrt{\frac{2m(V-E)}{\hbar^2}}$

22. Probability $P = \int_{-a}^{a} |\psi|^2 dx = \int_{-a}^{a}\left(\frac{\alpha}{\pi^{\frac{1}{2}}}\right)e^{-\alpha^2 x^2} dx$

Put $\alpha^2 x^2 = y^2$

$\alpha^2 2x\,dx = 2y\,dy$

$dx = \frac{y dy}{x\alpha^2} = \frac{\alpha x dy}{x\alpha^2} = \frac{dy}{\alpha}$.

$\therefore \quad P = \frac{1}{\pi^{\frac{1}{2}}}\int e^{-y^2} dx$

To find the limits

when $x = -a$, $y = -\alpha a = -\left(\frac{m\omega}{\hbar^2}\right)^{\frac{1}{2}} a$

But in the ground state, we have

$\frac{1}{2} m\omega^2 a^2 = \frac{1}{2}\hbar\omega$

$a = \sqrt{\frac{\hbar}{m\omega}}$

$\therefore \quad P = \frac{1}{\pi^{\frac{1}{2}}}\int_{-1}^{1} e^{-y^2} dy = \frac{2}{\pi^{\frac{1}{2}}}\int_0^1 e^{-y^2} dy$

$$P = \frac{2}{\pi^{\frac{1}{2}}}\int_0^1\left(1 - y^2 + \frac{y^4}{2!} - \frac{y^6}{3!} + \cdots\right)dy$$

$$P = \frac{2}{\pi^{\frac{1}{2}}}\left[y - \frac{y^3}{3} + \frac{y^5}{10} - \cdots\right]_0^1$$

$$P = \frac{2}{\pi^{\frac{1}{2}}}\left(1 - \frac{1}{3} + \frac{1}{10} - \frac{1}{42} + \cdots\right)$$

$P = 1.129 \times 0.7428 = 0.84$

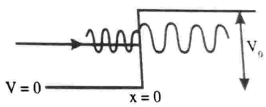
This problem shows that the probability of finding the oscillator outside the classical limit (–a to a) is 16%. This is the reason why wave function extends (ψ_0) beyond $-a$ and $+a$ while drawing $\psi_0(x)$ versus x. (see figure 4.14)

23. (a) $E > V_0$

In region I, $\psi_1 = Ae^{ikx} + Be^{-ikx}$

In region II, $\psi_2 = Ce^{ik'x}$

Where $k = \sqrt{\frac{2mE}{\hbar^2}}$ and $k' = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$

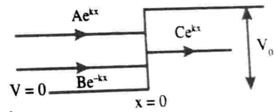


Boundary condition, $\psi_1|_{x=0} = \psi_2|_{x=0}$

$A + B = C$ ... (1)

$\left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0} \Rightarrow ik(A-B) = ik'C$

$A - B = \frac{k'}{k}C$ ... (2)



From (1) and (2)

$\Rightarrow \quad A = \frac{1}{2}\left(1 + \frac{k'}{k}\right)C$ and $B = \frac{1}{2}\left(1 - \frac{k'}{k}\right)C$

So, $\frac{B}{A} = \frac{k-k'}{k+k'}$ where, $\left[\frac{k'}{k} = \sqrt{1 - \frac{V_0}{E}}\right]$

(b) $\frac{B}{A} = \frac{1 - \sqrt{1 - \frac{V_0}{E}}}{1 + \sqrt{1 - \frac{V_0}{E}}} = 0.4 = \frac{2}{5} \Rightarrow \sqrt{1 - \frac{V_0}{E}} = \frac{3}{7} \Rightarrow \frac{V_0}{E} = \frac{40}{49} \Rightarrow \frac{E}{V_0} = \frac{49}{40} = 1.225$

Reflection, coefficient $R = \left|\frac{B}{A}\right|^2 = 0.16$

Transmission coefficient, $T = 1 - R = 1 - 0.16 = 0.84$.

24. (a) $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$

To find E_n, evaluate the expectation value of $\hat{H}$, where $H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V$, Here

$V = 0$ so $E_n = \langle H_n\rangle = \int_0^L \psi_n \hat{H}\psi_n dx = \frac{n^2h^2}{8mL^2}$

$$E_n = \frac{\hat{p}_n^2}{2m} = \frac{n^2h^2}{8mL^2} \Rightarrow \hat{p}_n = \frac{nh}{2L}$$

Let ϕ_n be the eigen function of momentum operator, then

$$\hat{p}\phi = p\phi$$

$$-i\hbar\frac{d}{dx}\phi = \frac{nh}{2L}\phi$$

Solving we get $\phi = Ae^{\frac{i\pi n x}{L}}$

(b) $\hat{p}_n\psi_n = -i\hbar\frac{d}{dx}\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$

$$\hat{p}_n\psi_n = -\frac{in\pi\hbar}{L}\cos n\frac{\pi x}{L}$$

Since $\hat{p}_n\psi_n \neq p_n\psi_n$, energy eigen functions are not eigen functions of the momentum operator.

25. For a particle of mass 'm' confined in a I-D box of length 'l', the wave function of the particle in n^{th} state, is

At $t = 0$, $\phi_n(x, 0) = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right)$

Energy eigenvalue, $E_n = \frac{n^2\pi^2\hbar^2}{2ml^2}$

For the given box, $l = 1$

So, $\phi_n(x, 0) = \sqrt{2}\sin(n\pi x)$

$$E_n = \frac{n^2\pi^2\hbar^2}{2m}$$

General state of the particle, $\psi_n(x, 0) = \sum_{n=1}^{\infty} C_n\phi_n(x, 0)$

$$\psi_n(x, t) = \sum_{n=1}^{\infty} C_n\phi_n(x, 0)e^{-\frac{iE_n t}{\hbar}}$$

Given wavefunction/state of the particle

$$\psi(x, 0) = A\sin 2\pi x\cdot\cos\pi x = \frac{A}{2}[\sin 3\pi x + \sin\pi x] = \frac{A}{2\sqrt{2}}\phi_3(x, 0) + \frac{A}{2\sqrt{2}}\phi_1(x, 0)$$

Applying normalization condition,

$$\int_0^{L=1} \psi^*(x, 0)\psi(x, 0)dx = 1$$

$$\Rightarrow \left(\frac{A}{2\sqrt{2}}\right)^2 + \left(\frac{A}{2\sqrt{2}}\right)^2 = 1 \quad \Rightarrow \boxed{A = 2}$$

So, $\psi(x, 0) = \frac{1}{\sqrt{2}}\phi_3(x, 0) + \frac{1}{\sqrt{2}}\phi_1(x, 0)$

(a) $\psi(x, t) = \frac{1}{\sqrt{2}}\phi_3(x, 0)e^{-iE_3t/\hbar} + \frac{1}{\sqrt{2}}\phi_1(x, 0)e^{-iE_1t/\hbar}$

where, $E_3 = \frac{9\pi^2\hbar^2}{2m}$, $E_1 = \frac{\pi^2\hbar^2}{2m}$

(b) $\langle E\rangle = P(E_1)\cdot E_1 + P(E_3)\cdot E_3 = |C_1|^2\cdot E_1 + |C_3|^2\cdot E_3$

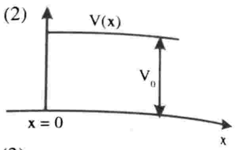
$$= \frac{1}{2}\times\frac{\pi^2\hbar^2}{2m} + \frac{1}{2}\times\frac{2\pi^2\hbar^2}{2m} = \frac{5\pi^2\hbar^2}{2m}$$

$$\langle p_x\rangle = \int_0^1 \psi^*(x, 0)\left(-i\hbar\frac{\partial}{\partial x}\right)\psi(x, 0)dx = 0$$

26. Time independent Schrodinger equation

$$\frac{d^2\psi}{dx^2}+\frac{2mE}{\hbar^2}\psi=0 \qquad \text{(Region - I)} \qquad \dots (1)$$

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}(E-V)\psi=0 \qquad \text{(Region - II)} \qquad \dots (2)$$



Putting $E=\frac{V_0}{2}$

$$\frac{d^2\psi}{dx^2}+\frac{mV_0}{\hbar^2}\psi=0 \text{ For region I} \qquad \dots (3)$$

$$\frac{d^2\psi}{dx^2}-\frac{mV_0}{\hbar^2}\psi=0 \text{ For region II} \qquad \dots (4)$$

Let $\frac{mV_0}{\hbar^2}=k^2$

So, $$\frac{d^2\psi}{dx^2}+k^2\psi=0 \qquad \dots (5)$$

$$\frac{d^2\psi}{dx^2}-k^2\psi=0 \qquad \dots (6)$$

Solution of (5) and (6)

$$\psi_1=Ae^{ikx}+Be^{-ikx} \qquad \dots (7)$$

$$\psi_2=Ce^{-kx}+De^{+kx} \qquad \dots (8)$$

Since, ψ_2 should be finite at $x=\infty$. So, $D=0$, $\psi_2=Ce^{-kx}$

Applying boundary condition,

$$\psi_1|_{x=0}=\psi_2|_{x=0}$$

$$A+B=C \qquad \dots (9)$$

$$\left.\frac{d\psi_1}{dx}\right|_{x=0}=\left.\frac{d\psi_2}{dx}\right|_{x=0} \Rightarrow A-B=iC \qquad \dots (10)$$

Adding (9) and (10)

$$A=\frac{1+i}{2}C$$

Subtracting (10) and (9)

$$B=\frac{1-i}{2}C$$

So, $\psi_1=\left(\frac{1+i}{2}\right)Ce^{ikx}+\left(\frac{1-i}{2}\right)Ce^{-ikx}$ Reflection coefficient, $R=\frac{|B|^2}{|A|^2}=1$

Transition coefficient, $T=1-R=0$

So, $R+T=1$

27. For a 3D cubical box $E=\frac{\hbar^2}{2ma^2}(n_x^2+n_y^2+n_z^2)$

Here $E=14\frac{\pi^2\hbar^2}{2ma^2}$

comparing, we get

$n_x^2+n_y^2+n_z^2=14$

This will be satisfied for

n_x	n_y	n_z
1	2	3
1	3	2
3	2	1
3	1	2
2	1	3
2	3	1

i.e., $E_{123}=E_{132}=E_{321}=E_{312}=E_{213}=E_{231}$

So, degeneracy is 6.

28. $\psi(x)=Cxe^{-bx}$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V\psi=E\psi \qquad \dots\dots (1)$$

$$\frac{d^2\psi}{dx^2}=-2bCe^{-bx}+b^2Cxe^{-bx}$$

put in eq (1)

$$\frac{-\hbar^2}{2m}(-2bCe^{-bx} + b^2Cxe^{-bx}) + V(x)Cxe^{-bx} = ECxe^{-bx}$$

Cancel Ce^{-bx} throughout

$$\frac{-\hbar^2}{2m}(-2b + b^2x) + x\,V(x) = Ex$$

or $\quad E = +\dfrac{\hbar^2 b}{mx} - \dfrac{\hbar^2 b^2}{2m} + V(x)$

Since E is constant, there should be no term on the R.H.S. containing x.

$$\therefore \quad \frac{\hbar^2 b}{mx} + V(x) = 0$$

$$\therefore \quad V(x) = -\frac{\hbar^2 b}{mx}$$

and $\quad E = \dfrac{-\hbar^2 b^2}{2m}$.